Modelling inorganic carbon system in Utö Baltic Sea

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Tiivistelmä

Maapallon ilmakehän hiilidioksidipitoisuus on noussut ihmisen toiminnan seurauksena. Jopa 30% ihmistoiminnan aiheuttamasta hiilidioksidista absorboituu meriin hilliten pitoisuuden nousua ilmakehässä. Meressä hiilidioksidi liukenee veteen muodostaen hiilihappoa (H_2CO_3), mikä dissosioituu bikarbonaatiksi (HCO_3^-) ja karbonaatiksi (CO_3^{2-}). Näiden komponenttien suhteelliset osuudet riippuvat monista tekijöistä ja vaikuttavat veden pH-arvoon. Hiilidioksidin osuuden kasvaessa pH alenee ja meret happamoituvat. Jotta voitaisiin arvioida merien kykyä absorboida hiiltä tulevaisuudessa, on tärkeää ymmärtää meren karbonaattisysteemin toiminta ja siihen vaikuttavat tekijät. Myös happamoitumisen vaikutusta meren ekosysteemeihin tutkittaessa tarvitaan tietoa happamoitumisnopeudesta.

Tässä työssä tutkittiin karbonaattisysteemiä Itämerellä mittaamalla merivedestä pH, hiilidioksidin osapaine (pCO_2), alkaliniteetti ja liuennut epäorgaaninen hiili (DIC) Utön merentutkimusasemalla. Teoriassa kahden edellä mainitun komponentin avulla voidaan mallintaa koko karbonaattisysteemi. Meriveden pH ja pCO_2 mitattiin aseman jatkuvatoimisilla mittauslaitteilla. Alkaliniteetti ja DIC mitattiin vesinäytteistä, jotka kerättiin keväällä ja kesällä 2017 noin viikon mittaisten kampanjoiden aikana. Näytteet otettiin kolme kertaa vuorokaudessa klo 7, 13 ja 19 paikallista aikaa. Tutkimus suoritettiin Suomen Ympäristökeskuksessa. Mittauskampanjat olivat osa kansainvälistä JERICO NEXT projektia.

Mitatut karbonaattisysteemin komponenttien arvot tukivat aikaisempia mittauksia Itämerellä. Alkaliniteetti ja DIC korreloivat vahvasti keskenään sekä saliniteetin kanssa. Meriveden pH:n ja pCO_2:n välillä puolestaan oli selvä käänteinen riippuvuussuhde. Hiilidioksidin osapaine oli koko kevään ja kesän ajan elokuun puoliväliin saakka ilmakehän hiilidioksidipitoisuutta pienempi eli meri toimi hiilinieluna. Lisämittauksia tarvittaisiin, jotta saataisiin dataa muiltakin vuodenajoilta.

Mitattujen komponenttien avulla mallinnettiin karbonaattisysteemiä valtameriolosuhteisiin kehitellyllä CO2calc–ohjelmalla. Itämeren suuri valuma-alue ja jokien tuoma orgaaninen aines sekä olosuhteiden suuret paikalliset ja ajalliset vaihtelut aiheuttavat haasteita mallinnukselle. Parhaat mallinnustulokset saatiin, kun toinen mitattu muuttuja oli pH tai pCO_2 ja toinen alkaliniteetti tai DIC. Tällöinkin mallinnustuloksiin on suhtauduttava varauksella. Parhaan kuvan saamiseksi karbonaattisysteemistä Itämerellä on mitattava kaikki neljä komponenttia. Mallia voisi kehittää paremmaksi ottamalla huomioon alkaliniteetin orgaanisen komponentin sekä boorin määrän vaihtelut Itämeren osissa.

Avainsanat
Itämeri, karbonaattisysteemi, alkaliniteetti, epäorgaaninen kokonaishiili, pH, hiilidioksidin osapaine

Ohjaaja
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Säilytyspaikka

Muita tietoja

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Abstract

Anthropogenic carbon dioxide (CO_2) emissions have raised the CO_2 content of the atmosphere radically during the last 200 years. Currently, around 30% of anthropogenic CO_2 gas is absorbed by the oceans thus mitigating the rise of the CO_2 content in the atmosphere. In water, CO_2 dissolves and forms carbonic acid (H_2CO_3), which dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Ratio of these components, which depends on various factors, influences on the pH of the water. When the proportion of CO_2 in the water increases, pH decreases. As a result, the oceans acidify. Understanding function of marine inorganic carbon system and the factors affecting it is essential to estimate the oceans' ability to absorb CO_2 in the future. Also, rate of acidification must be evaluated when studying the effects of acidification on marine ecosystems.

The aim of this research was to examine inorganic carbon system in the Baltic Sea by measuring seawater pH, partial pressure of carbon dioxide (pCO_2), alkalinity and dissolved inorganic carbon (DIC) at Utö Atmospheric and Marine Research Station. In theory, inorganic carbon system can be modelled with two out the four components mentioned above. Seawater pH and pCO_2 were measured by continuous measurement equipment. Alkalinity and DIC were measured using discrete water samples during four week-long campaigns in spring and summer in 2017. Samples were taken three times a day at 7am, 1pm and 7pm local time. The study was performed at Finnish Environment Institute. Measurement campaigns were part of international research programme JERICO NEXT.

Measured values of carbonate system components support earlier results in the Baltic Sea. Alkalinity and DIC were strongly correlated. Also, both components correlated tightly with salinity. As for pH and pCO_2, those were clearly inversely related. Seawater pCO_2 was below the atmospheric content of CO_2 during the spring and summer until mid-August. In other words, the sea acted as a carbon sink. Additional measurements are needed to get data from all the seasons.

With measured components inorganic carbon system calculations and modelling were performed by CO2calc software. This software is designed for conditions in oceans. Large catchment area with DOM-rich river runoffs, hydrographical features, eutrophication and large seasonal changes makes Baltic Sea difficult to model. Best results were obtained when modelling was performed with one discrete measurement (A_T or DIC) and one continuous measurement (pH or pCO_2). Even then, modelling results should be used with cation. Therefore, it would be best to measure all the four components to get the most accurate picture of the inorganic carbon system. Model could be improved for Baltic Sea conditions by taking account organic alkalinity and correct estimate for borates.

Keywords
Baltic Sea, inorganic carbon system, alkalinity, dissolved inorganic carbon, pH, partial pressure of carbon dioxide

Supervisor
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Additional information

CONTENTS:

ABBREVIATIONS

A_{Gran}	Total alkalinity defined by Gran method
a_H+	Hydrogen ion activity
A_{OLS}	Total alkalinity defined by ordinary least square method
A_C	Carbonate alkalinity
A_T	Total alkalinity
C_T	Total dissolved inorganic carbon
CV	Coefficient of variation
DIC	Total dissolved inorganic carbon
DOM	Dissolved organic matter
fCO_2	Fugacity of carbon dioxide
K_0	Solubility coefficient for CO_2
K_1	Dissociation constant for H_2CO_3*
K_2	Dissociation constant for HCO_3^-
K_F	Dissociation constant for HF
K_{SO4}	Dissociation constant for HSO_4^-
K_{sp}	Solubility product
K_W	Ion product of water
mCP	pH dependent indicator meta-Cresol Purple
pH_{NBS}	Practical pH scale, developed by National Bureau of standards, USA
pH_{SWS}	Seawater scale for pH
pH_T	Total scale for pH
pCO_2	Partial pressure of carbon dioxide
TCO_2	Total dissolved inorganic carbon
γ	Activity coefficient
ΣCO_2	Total dissolved inorganic carbon
Ω	Degree of saturation (ratio between the actual product of the concentrations and solubility product)
[x]	Concentration of x

1 INTRODUCTION

Anthropogenic carbon dioxide (CO_2) emissions have raised the CO_2 content of the atmosphere radically during the last 200 years (Hartmann et al., 2013). As Arrhenius (1896) suggested over a century ago, the atmospheric concentration of carbon dioxide as well as other greenhouse gases have an influence on climate and global average temperature. According to datasets, globally averaged combined land and ocean surface temperature has risen 0.85 °C [0.65 to 1.06] °C in years 1880–2012 (Hartmann et al., 2013). The influences of climate change differ spatially. Some expected effects include sea level rise, changes in ecosystems, extreme weather events, species extinctions and spread of tropical diseases.

Mostly due to fossil fuel burning and deforestation CO_2 is nowadays the most significant anthropogenic greenhouse gas (Figure 1). Methane (CH_4) as well as nitrous oxide (N_2O) emissions are also rising, but their abundance is still much smaller compared to CO_2.

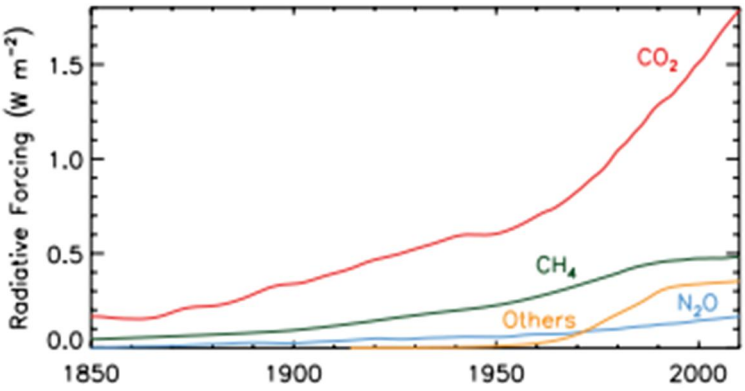

Figure 1. Radiative forcing from major anthropogenic greenhouse gases and groups of halocarbons ("others") from 1850 to 2011 (Myhre et al., 2013).

Global carbon cycle contains reservoirs of carbon, which are connected by exchange fluxes of carbon (Figure 2). Some reservoirs are said to be fast. In other words, those have relatively rapid reservoir turnover times and are influenced by large exchange fluxes. Atmosphere, oceans and freshwaters, vegetation and soils belong to fast reservoirs and they have turnover times from a few years to millennia. Slow carbon reservoirs consist of

massive carbon stocks in rocks and sediments. Turnover times for these mainly geological reservoirs are at least 10,000 years. Fossil fuel consumption has changed the situation. Carbon from slow geological reservoirs has been transferred to fast reservoirs. That has led to changes in the reservoirs and especially the quantity of carbon in the atmosphere and in the oceans has increased.

Atmospheric carbon has a turnover time of only a few years. Atmospheric reservoir contains 830 PgC and it has risen 240 PgC from preindustrial time. Land vegetation maintains a carbon storage from 420 to 620 PgC (Prentice et al., 2001) and soils from 1,500 to 2,400 PgC (Batjes, 1996). A carbon stock of about 1,700 PgC lies in permafrost soils (Tamocai et al., 2009).

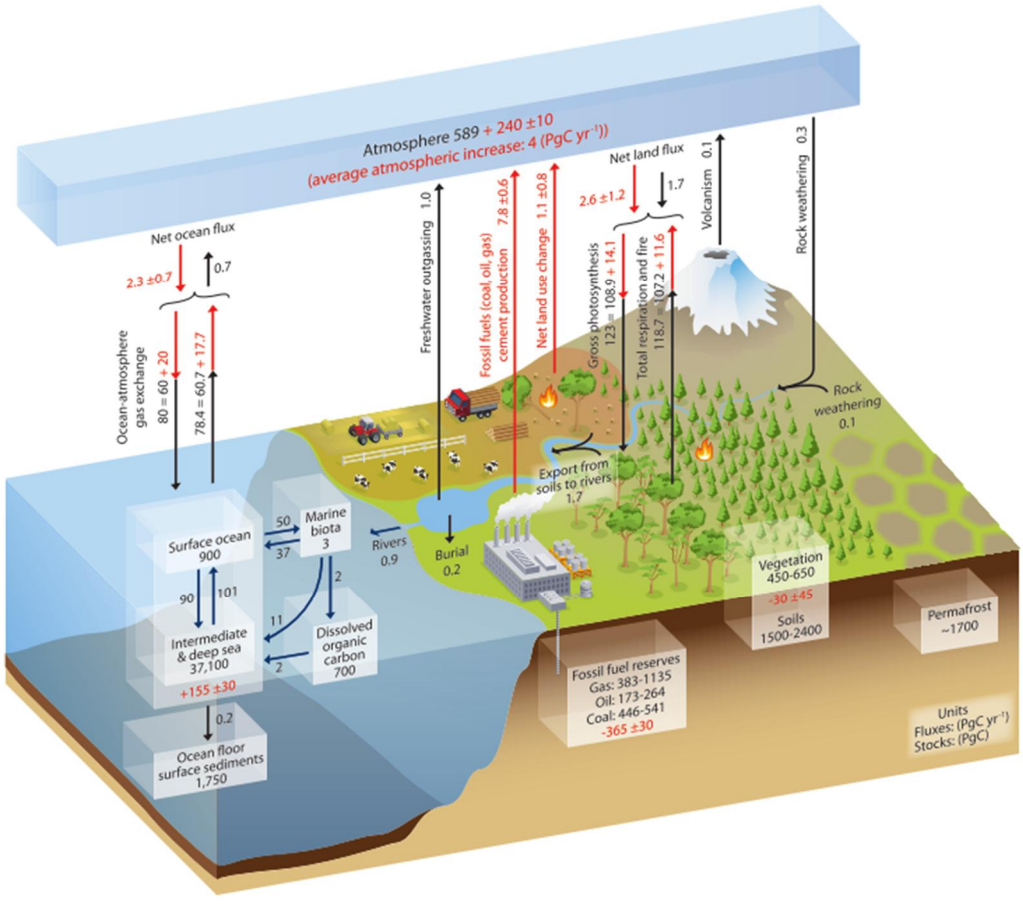

Figure 2. Simplified graphic of the global carbon cycle. Numbers represent carbon stocks in PgC and annual carbon exchange fluxes in PgC per year. Black numbers and arrows refer to time before Industrial Era (about 1750). Red arrows and numbers indicate anthropogenic fluxes averaged over the years 2000–2009. Red numbers in the reservoirs indicate the change in the reservoir over the period 1750–2011 (Ciais et al., 2013).

In the ocean, carbon appears mostly as Dissolved Inorganic Carbon (*DIC*). The oceanic carbon stock is much larger than atmospheric or terrestrial ones with about 38,000 PgC. Small amount of carbon in ocean is present as Dissolved Organic Carbon (DOC, ~700 PgC) and a small organic carbon pool of phytoplankton and other microorganisms (~3 PgC). Carbon in fossil fuel reserves has lessened about 365 PgC while atmospheric and oceanic reserves have accumulated (240 PgC and 155 PgC respectively) over the Industrial Period 1750-2011.

The tropospheric content of CO_2 has been regularly monitored since 1958 at Mauna Loa, Hawaii (Keeling et al., 2009). Information about earlier CO_2 content has been reconstructed from ice core records (Neftel et al., 1994). Preindustrial level was 280 ppm and during the last 600 000 years the CO_2 content of the atmosphere has varied between 180 and 300 ppm (Barnola *et al.*, 1987; Neftel *et al.*, 1994; Siegenthaler *et al.*, 2005; Figure 3). Content of CO_2 in December 2017 at Mauna Loa was 407.62 ppm (NASA, 2018). Caldeira and Wickett (2003) have evaluated that in year 2300 CO_2 content may rise as high as 2,000 ppm assuming, that all remaining fossil fuels will be burned.

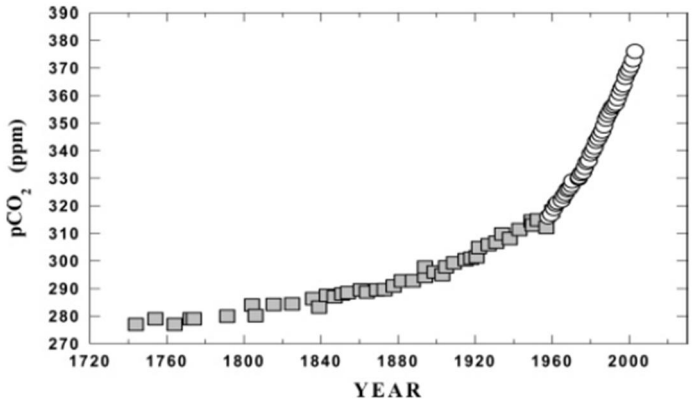

Figure 3. Atmospheric carbon dioxide from 1720 to 2000 at Hawaii (Millero, 2007). Data from the atmospheric measurements (circles) (Keeling et al., 2009) and analysis of the air trapped in ice cores (squares) (Neftel et al., 1994)

1.1 CARBON PUMPS

At the air-sea interface, carbon dioxide is constantly moving in or out of the water. In water, CO_2 dissolves and forms carbonic acid (H_2CO_3), which dissociates into bicarbonate

(HCO_3^-) and carbonate (CO_3^{2-}). Ratio of these components, which depends on various factors, influences on the pH of the water. Currently, around 30% of anthropogenic CO_2 gas is absorbed by the oceans thus mitigating the rise of the CO_2 content in the atmosphere (Khatiwala et al., 2013). High solubility cold waters in high latitudes are enriched with CO_2. This heavy water sinks to the depths of the ocean taking CO_2 to oceans interior. Meridional Overturning Circulation (MOC) acts as a conveyor belt transporting water masses. This physico-chemical process transferring CO_2 from the atmosphere to the oceans is called the "solubility pump" (Volk and Hoffert, 1985).

Biological processes in the ocean also have an influence on carbon cycle. Phytoplankton binds CO_2 through photosynthesis. Some of that carbon sinks as dead organisms and particles. Most of the sinking particles are recirculated by bacteria back to surface as *DIC*. However, part of the carbon flux ends up in abyssal depths and deep ocean sediments. This pull down of surface pCO_2 is called a "soft-tissue pump" (Volk and Hoffert, 1985).

Some marine organisms form calcium carbonate shells ($CaCO_3$) from Ca^{2+} and CO_3^{2-} ions. Biogenic $CaCO_3$ appears in two crystal structures: calcite and aragonite. The solubility product K_{sp} for $CaCO_3$ is the product of Ca^{2+} and CO_3^{2-} concentrations in saturated solution (Morse and Mackenzie, 1990):

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \quad (1)$$

K_{sp} depends on the crystal structure, salinity, pressure and temperature. Degree of saturation Ω is defined as the ratio between the actual product of the concentrations and solubility product (Morse and Mackenzie, 1990):

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{K_{sp}} \quad (2)$$

Generally, ocean surface waters are oversaturated with calcite. Calcifying organisms are able to build $CaCO_3$ shells even in undersaturated waters and overcome magnesium ion inhibition of $CaCO_3$ precipitation. Dead organisms sink taking $CaCO_3$away from surface water circulation. Solubility of $CaCO_3$ increases with pressure and therefore $CaCO_3$ dissolutes in deep waters. This process is called "carbonate pump" and together with soft-tissue pump they are referred as "biological pump" (Volk and Hoffert, 1985).

Uptake of CO_2 by the oceans cannot be measured directly and must be estimated. Sediment records give some idea of the past values in the oceans, but those are not as accurate as the ice core records for atmospheric CO_2 (Millero, 2007).

1.2 OCEAN ACIDIFICATION

Rising atmospheric CO_2 content raises the proportion of CO_2 in the water. As a result, the oceans acidify (Doney et al., 2009). In the estimation of Caldeira and Wickett (2003) ocean pH may reduce 0.7 units by the year 2200 if all the remaining fossil-fuel resources will be burnt. Acidification threatens marine organisms, especially calcifying organisms such as corals, coccolithophorides, foraminifera and pteropods (Hofmann et al., 2010). Coral reefs form important ecosystems providing feeding ground and nursery for other organisms. Coral reef decline affects thus many related organisms. Reef corals can do some regulation to the pH of their internal calcifying fluid. The regulation is shown to depend on *DIC* and A_T as well as pH of the seawater (Comeau et al., 2017). Single-celled coccolithophorides and foraminifera play an important role in sustaining the biological carbon pump. Those account for the major part of biogenic calcification. So, in addition to changes in food web, the loss of coccolithophorides and foraminifera may also change the operation of the biological carbon pump (Wolf-Gladrow et al., 1999).

Also, ocean acidification is expected to change the metal ion speciation. For example, the amount of bioavailable iron was shown to be inhibited by acidification (Shi et al., 2010). Rising atmospheric CO_2 will probably reduce marine trace gas emissions. Hopkins et al (2010) observed significantly reduced methyl iodide and dimethylsulfide contents in their mesocosm experiment simulating atmospheric CO_2 content of 750 ppm. Also, large reductions in other iodocarbons contents were noticed. That will potentially reduce planetary albedo and enhance global warming for marine trace gases contribute to the formation of cloud condensation nuclei.

1.3 OBJECTIVES OF THIS THESES

JERICO NEXT (Joint European Research Infrastructure network for Coastal Observatory – Novel European eXpertise for coastal observaTories) is a 4-year project funded by European Commission and it extends work started with the project JERICO (FP7). JERICO NEXT aims at improving the cooperation in coastal observatories in Europe and providing researchers with continuous and more valuable coastal data linking physical and

biological information. The project involves 33 expert partners from 15 European countries including Finnish Environment Institute and Finnish Meteorological Institute (Durand et al., 2016).

This work is done for Work Package 4 of JERICO NEXT for the task Joint Research Activity Project 5 (JRAP-5) which is titled "*Coastal carbon fluxes and biogeochemical cycling*". The main target of JRAP-5 is to "understand and quantify the effect of biological activity on carbon release or uptake, relative to physical and chemical processes affecting sea-air carbon fluxes". This JRAP provides information for developing optimal observation network for carbon flux studies as well as concepts and methods towards harmonized measurements. Observations include pCO_2, alkalinity and pH and development of relevant biological methods is supported.

JRAP-5 will cover time ranges of few minutes up to one year and spatial resolution from few hundred meters up to more than a thousand kilometres. The conditions vary from Arctic Ocean on Svalbard to brackish water Baltic Sea and to warm and saline waters of Aegean Sea in Greece (Figure 4).

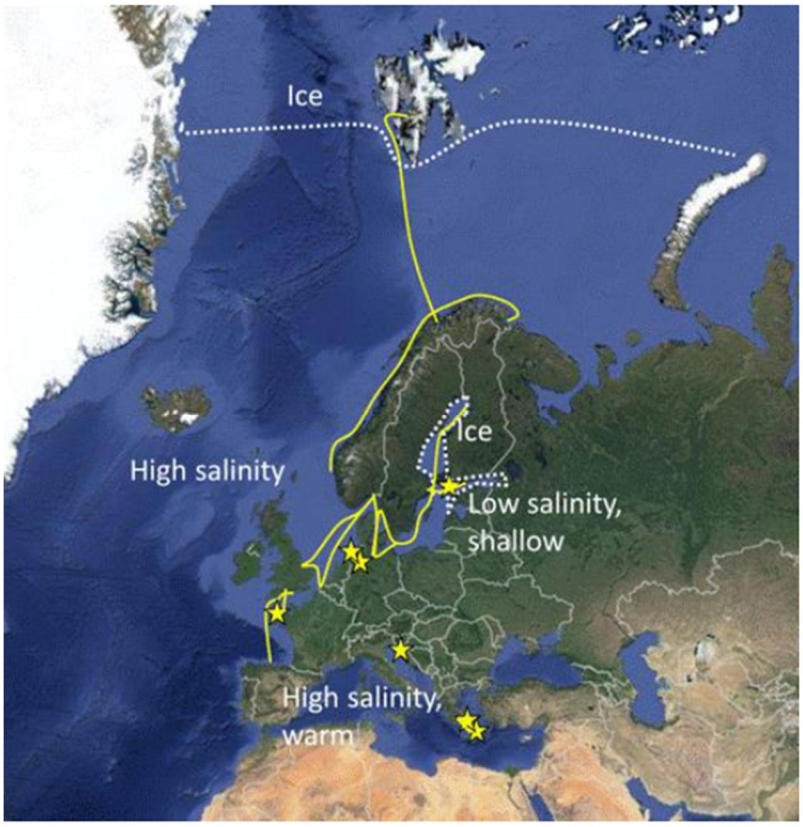

Figure 4. Jerico Next JRAP5 measuring sites (Durand et al., 2016)

The scientific focus is in biological processes coupled with carbon cycle and how these processes vary in different European coastal sea areas. Physical (temperature, salinity, mixing etc.), chemical (carbonate system) and biological (biomass, production) measurements are combined to get a better picture of the driving forces of air-sea carbon fluxes in these environments. Study locations represent different kind of environmental conditions so that the influence of some specific conditions (like salinity and temperature gradients, ice covers, phytoplankton blooms) to the fluxes could be observed.

The main objective of this thesis is to study inorganic carbon system in Utö, Baltic Sea. Target is to notice how measuring equipment in Atmospheric and Marine Research Station works for carbonate system studies. The accuracies and precisions of the measurements are evaluated. Especially the function of the continuous measurements (pH, pCO2) is significant to get data with high temporal resolution in the future. Also, purpose is to evaluate with which two measured components the carbonate system of the Baltic Sea is most reliably modelled and to identify how different factors (temperature, salinity) influence on the inorganic carbon system and its components.

2 INORGANIC CARBON SYSTEM

2.1 INORGANIC CARBON SYSTEM

Carbon dioxide flux at air–sea interface flows from larger content towards lower content according to Henry's Law. Surface water strives to be thermodynamically balanced with the atmosphere (Henry, 1803):

$$[CO_2^*] = K_0 pCO_{2Air} \quad (3)$$

where pCO_{2Air} is atmospheric partial pressure of CO_2, K_0 is solubility constant of CO_2 and $[CO_2^*]$ is concentration of dissolved CO_2 and H_2CO_3 in water. Equilibration process and CO_2 flux between air-sea interface is increased with wind speed (Wanninkhof, 1992) and depend also on precipitation, heat flux and sea ice.

Globally the oceans act as carbon sinks, but locally water environment acts as a carbon source or sink depending on the situation. Ocean circulation controls the dispersal of the CO_2 into the ocean interior. Cold water can uptake more CO_2 than warmer water. Therefore, in high latitudes the surface water holds more CO_2 than in lower latitudes. Deep water formation in high latitudes transports CO_2 rich water along deep water circulation (Falkowski et al., 2000).

In water dissolved inorganic carbon is present in four forms: dissolved CO_2, carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). Ratio of these components depends on various factors including pH (Figure 5). Carbonic acid, bicarbonate and carbonate cannot be measured separately. However, the sum of all dissolved inorganic carbon (*DIC*) as well as total alkalinity (A_T), pH and pCO_2 can be measured and with these components the carbonate system can be modelled.

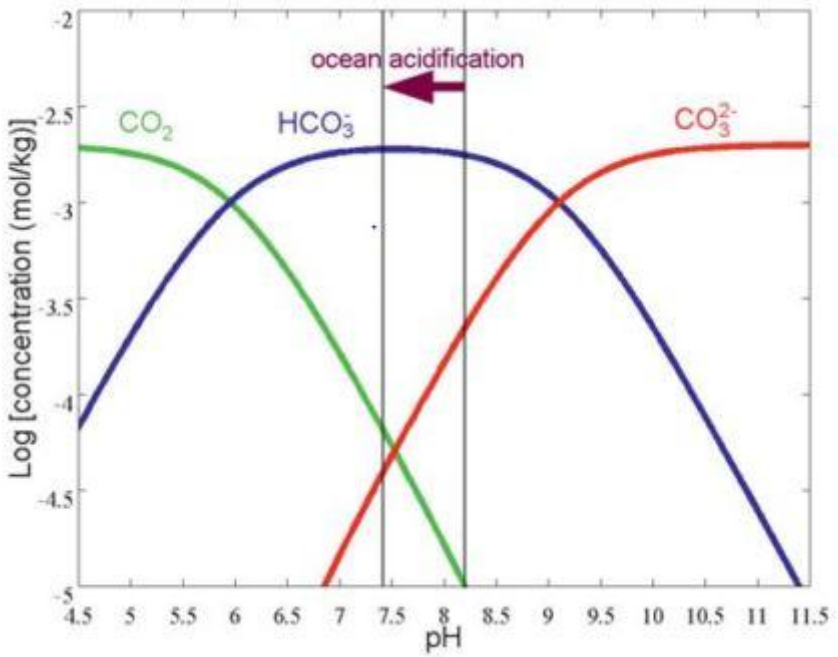

Figure 5. Bjerrum plot. Concentration of the components of the ocean carbonate system versus pH. Calculated with *DIC* = 2100 µmol L^{-1}, S = 35 PSU and T = 25 °. The purple arrow shows the effect of decline of pH to the system (Hofmann and Schellnhuber, 2010).

2.2 PARTIAL PRESSURE OF CO_2

Dissolved CO_2 and carbonic acid together have a share under 1 % of the total dissolved inorganic carbon in usual marine conditions. Those are also analytically identical. Therefore, CO2 and H_2CO_3 are usually treated together (Stumm and Morgan, 1996)

$$pCO_2(aq) = [CO_2] = [CO_2(aq)] + [H_2CO_3] \quad (4)$$

Because CO_2 does not act precisely like an ideal gas, the term fugacity of carbon dioxide (fCO_2) is sometimes used instead of partial pressure (pCO_2). Fugacity represents active partial pressure and it is about 3-4% smaller than pCO_2.

In addition to gas exchange with the atmosphere, carbon dioxide is released into and taken from water according to biological processes. Respiration and decomposition increase CO_2 content and assimilation reactions consume CO_2 from the water.

Surface water pCO_2 is measured on air equilibrated with the seawater. Equilibration system may be either passive or active and manual or automatic (Kyung Yoon et al., 2016).

Equilibrated air is then analysed with chromatography system or presently more often with infrared detector. The system must be calibrated with standard gases in every hour or so.

2.3 DISSOLVED INORGANIC CARBON

Dissolved inorganic carbon (*DIC*) is the sum of all dissolved carbon in water (Stumm and Morgan, 1996):

$$DIC = [CO_2] + [HCO_3^-] + [CO_3^{2-}] \quad (5)$$

In literature, *DIC* is termed also C_T, TCO_2 and ΣCO_2.

DIC is produced through respiration, weathering and mineralization of organic matter in soils and water. Rivers transport *DIC* and organic matter from terrestrial ecosystems to the sea. Also, the sea currents transport *DIC* and organic matter within the sea.

DIC can be measured by potentiometric, coulometric and spectrometric methods. In coulometric and spectrometric methods phosphoric acid (H_3PO_4) or nitric acid (HNO_3) is added to the sample. Sample acidifies and eventually all the *DIC* of the sample appears as CO_2. Carrier gas is used to strip the CO_2 out of the solution and CO_2 is measured.

SOMMA (Single-operator multiparameter metabolic analyzer) system was developed for high precision *DIC* measurements (Johnson et al., 1993, 1985; Johnson and Sieburth, 1987). Stripped CO_2 is lead to a solution with ethanolamine, which reacts with CO_2. *DIC* is then determined by coulometric titration. Infrared absorption system has made also spectrometric determination of CO_2 very accurate and precise (Baer et al., 2002).

2.4 SEAWATER PH

Acidity of aqueous solution is expressed by pH. The original definition of pH by Sørensen (1909) was the negative logarithm to base 10 of hydrogen ion concentration:

$$pH = -log[H^+] \quad (6)$$

More correctly, pH is defined as the negative logarithm of hydrogen ion activity a_{H^+}. Hydrogen ion activity is related to its concentration [H^+] by the activity coefficient γ (Stumm and Morgan, 1996):

$$pH = -\log(a_{H^+}) = -log(\gamma[H^+]) \quad (7)$$

Traditionally pH has been measured by potentiometer, which measures the electrical potential difference between the reference electrode and pH electrode. This difference depends on hydrogen ion activity. Potentiometer must be calibrated with buffer solutions of known pH. National Bureau of Standards (NBS, USA) developed a practical pH scale or NBS scale pH_{NBS} with reference buffer solutions. The ionic strength of the references is only 0.1, which makes the suitability of the scale for seawater (ionic strength about 0.7) questionable.

In addition to NBS scale other scales have been developed considering seawater. Total scale (pH_T) is based on reference series made in artificial seawater containing hydrogen sulphate (HSO_4^-) which is abundant in seawater (Dickson, 1984; Hansson, 1973a):

$$[H_T^+] = [H_F^+] + [HSO_4^-] \quad (8)$$

H_F^+ indicates free hydrogen ions. Seawater scale (pH_{SWS}) takes into account besides sulphate also fluoride (F^-) (Dickson and Millero, 1987; Dickson and Riley, 1979):

$$[H_{SWS}^+] = [H_F^+] + [HSO_4^-] + [HF] \quad (9)$$

The influence of fluoride is small compared to hydrogen sulphate and the difference of these scales is very small. Both scales need different reference buffers for different salinities. That is not a problem in oceanic measurements when the salinity is quite stable, but in coastal areas and estuaries like Baltic Sea the salinity gradient is large, and the use of these scales is difficult.

At 20° C and salinity of 35 the difference between pH_T and pH_{SWS} is about 0.01 units and pH_{NBS} differs from pH_T about one decimal. When pH is used to describe environmental circumstances, the choice of scale is not significant. However, in inorganic carbon system studies it is very important.

A precise method for measuring pH was developed with indicators that absorb light, for instance m-cresol purple and thymol blue (Clayton and Byrne, 1993; Robert-Baldo et al., 1985). Spectrophotometric measurement is also fast compared to potentiometer. Reagent is added to the sample and absorbances at wavelengths of maximum for the protonated and

deprotonated forms of the reagent is measured. With known molar absorptivities of the reagent pH of the sample can be calculated.

2.5 TOTAL ALKALINITY

Total alkalinity (A_T) is a measure of acid-binding or buffer capacity of the water. It is defined by the excess of proton acceptors over proton donors (Dickson et al., 2007):

$$\begin{aligned} A_T = {} & [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] \\ & + [SiO(OH)_3^-] + [NH_3] + [HS^-] - [H^+]_F - [HF] - [HSO_4^-] \\ & - [H_3PO_4] + [minor\ bases - minor\ acids] \end{aligned} \tag{10}$$

A_T controls how much of the excess CO_2 in atmosphere seawater can locally uptake by determining how many of the formed protons are neutralized. The higher A_T, the more CO_2 can be absorbed and the smaller is the impact on seawater pH. A_T is a conservative quantity with respect to temperature and pressure changes. Some of the alkalinity components like carbonates are non-conservative, but together the components act conservatively, although the share of the components can vary. When two water parcels are mixed, alkalinity obeys linear mixing relationships like salinity (Wolf-Gladrow et al., 2007).

Alkalinity is mostly determined by the quantity of bicarbonate and carbonate ions. Sometimes carbonate alkalinity A_C is used instead of A_T

$$A_C = [HCO_3^-] + 2[CO_3^{2-}] \tag{11}$$

Oceanic surface alkalinity is quite stable the biggest impacts coming from evaporation and precipitation. In coastal areas alkalinity is influenced by riverine alkalinity fluxes, $CaCO_3$ formation and denitrification.

Total alkalinity can be determined by titration with hydrochloric acid (HCl) to the carbonic acid end point. A_T is then computed from the titration curve using for instance a least-squares procedure based on a non-linear curve fitting approach (e.g. Dickson 1981) or on a modified Gran approach (Gran, 1952).

2.6 MODEL FOR INORGANIC CARBON SYSTEM

DIC components H_2CO_3, HCO_3^- and CO_3^{2-} cannot be measured separately. However, inorganic carbon system can be modelled with measurable components *DIC*, A_T, pH and pCO_2 with following equations (Stumm and Morgan, 1996):

$$\gamma[H^+] = 10^{-pH} \tag{12}$$

$$[OH^-] = \frac{K_W}{[H^+]} \tag{13}$$

$$[HCO_3^-] = \frac{K_1[CO_2]}{[H^+]} \tag{14}$$

$$[CO_3^{2-}] = \frac{K_2[HCO_3^-]}{[H^+]} \tag{15}$$

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] + [other\ bases - other\ acids] \tag{10}$$

$$DIC = [HCO_3^-] + [CO_3^{2-}] + [CO_2] \tag{5}$$

With these equations all the carbonate components can be calculated by two components out of *DIC*, A_T, pH and pCO_2 (Figure 6). K_w is ion product of water. Dissociation constants K_1 and K_2 depend on temperature, pressure and salinity. Values for dissociation constants in different salinities and temperatures have been determined experimentally by various researchers and those differ a little bit (Dickson and Millero, 1987; Goyet and Poisson, 1989; Hansson, 1973b; Lueker et al., 2000; Mehrbach et al., 1973; Millero, 2010; Roy et al., 1993). Choices of equilibrium constants as well as pH scale are significant in carbonate system modelling.

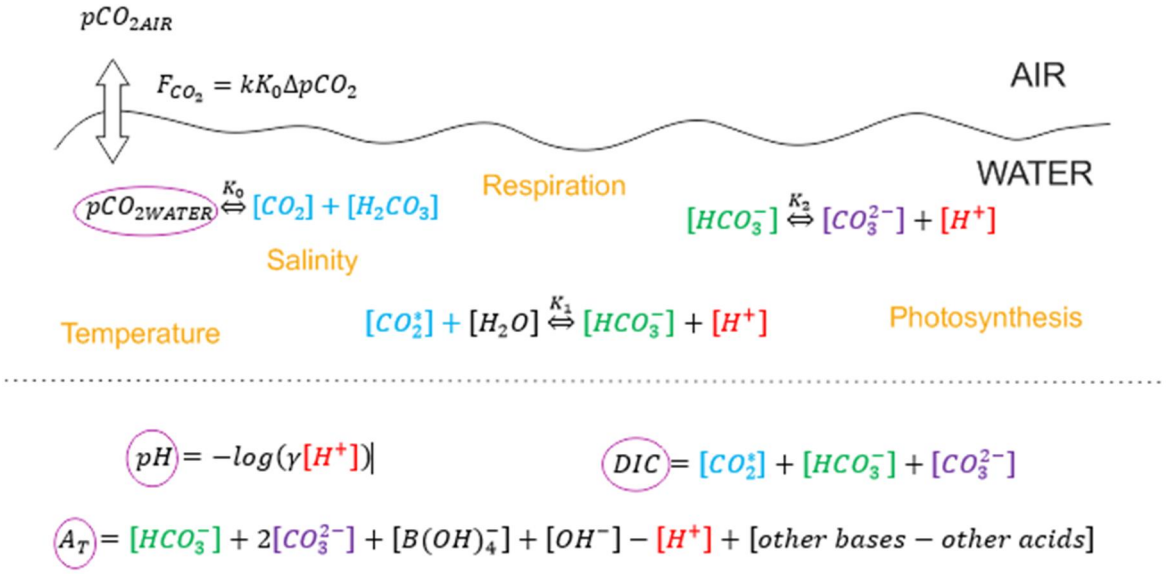

Figure 6. Inorganic carbon system. *At* the air-sea interface, carbon dioxide is constantly moving in or out of the water. Air-sea interface flux depends on gas transfer velocity (k), solubility constant of CO_2 (K_0) and the difference between the pressure of CO_2 in atmosphere and water. In water, CO_2 dissolves (blue) and forms carbonic acid (H_2CO_3, blue) which dissociates into bicarbonate (HCO_3^-, green) and carbonate (CO_3^{2-}, purple). K_1 and K_2 are dissociation constants. Measurable components *DIC*, A_T, pH and pCO_2 are encircled.

2.7 BALTIC SEA

Baltic Sea is a unique ecosystem with brackish water and scanty species. Therefore, it is very sensitive to environmental changes. At least 6,000 species (not including bacteria) lives in Baltic Sea (Ojaveer et al., 2010). Most of them are either euryhaline marine species or fresh water species. Only few brackish water species exists in this young sea. The composition of communities varies greatly in different parts of the Baltic Sea depending on salinity and temperature and other environmental factors.

Baltic Sea lies on the continental shelf in the northern Europe and is very shallow with mean depth approximately 60 meters. Its surface area is about 415 000 km^2 and a volume about 21 700 km^3. The catchment area includes about 85 million people and 14 countries with the area around four times the size of Baltic Sea itself (Lääne et al., 2005).

In Baltic Sea, the salinity and temperature gradients decrease from southwest to northeast (Feistel et al., 2009; Ojaveer et al., 2010). The surface salinity at the Kattegat area is about 30 whereas in the Finnish coast the salinity varies from 0.5 to 6. The water column is also stratified. Permanent halocline is located at 70–100 m. Thermocline usually occurs above the halocline. Seasonal variation in temperature is great and northern part typically gets an ice cover during the winter.

Phytoplankton abundance varies by seasons from very low concentrations in winter to high seasonal spring and summer blooms (up to 20µg L^{-1} of chlorophyll a). Physical and chemical factors affect to the magnitude and spatial structure of the blooms. Occasionally, high load of organic matter and decomposition of algal blooms cause periods or areas which are net-heterotrophic. This kind of biological activity gradients results in very large fluctuations in pCO_2 (100–1100 ppm) and pH (6.4–9.4) in Baltic Sea (Omstedt et al., 2010; Saderne et al., 2013; Schneider, 2011; Schneider and Müller, 2018).

2.7.1 Inorganic carbon system in Baltic Sea

Carbonate system of Baltic Sea has been investigated already a hundred years ago. Finnish chemist and marine researcher Kurt Buch (1917, Figure 7) performed pioneering work in this field with measurements of alkalinity, pH, pCO_2 and *DIC*. Baltic Sea inorganic carbon system was studied comprehensively until the Second World War, which interrupted the measurements. At present, climate change has made carbonate studies very relevant and from the mid- 1990s carbonate components of the Baltic Sea have been measured regularly (Hjalmarsson et al., 2008; Müller et al., 2016; Schneider and Müller, 2018; Thomas and Schneider, 1999).

Baltic Sea becomes undersaturated with respect to aragonite and calcite in winter. That may be the reason for scarcity of calcifying plankton such as coccolithophores in Baltic Sea except for the transition area with North Sea. Even though the water is oversaturated with calcite in summer, the calcium carbonate shells may dissolute in winter. Thus, carbonate pump is not significant in Baltic Sea (Tyrrell et al., 2008).

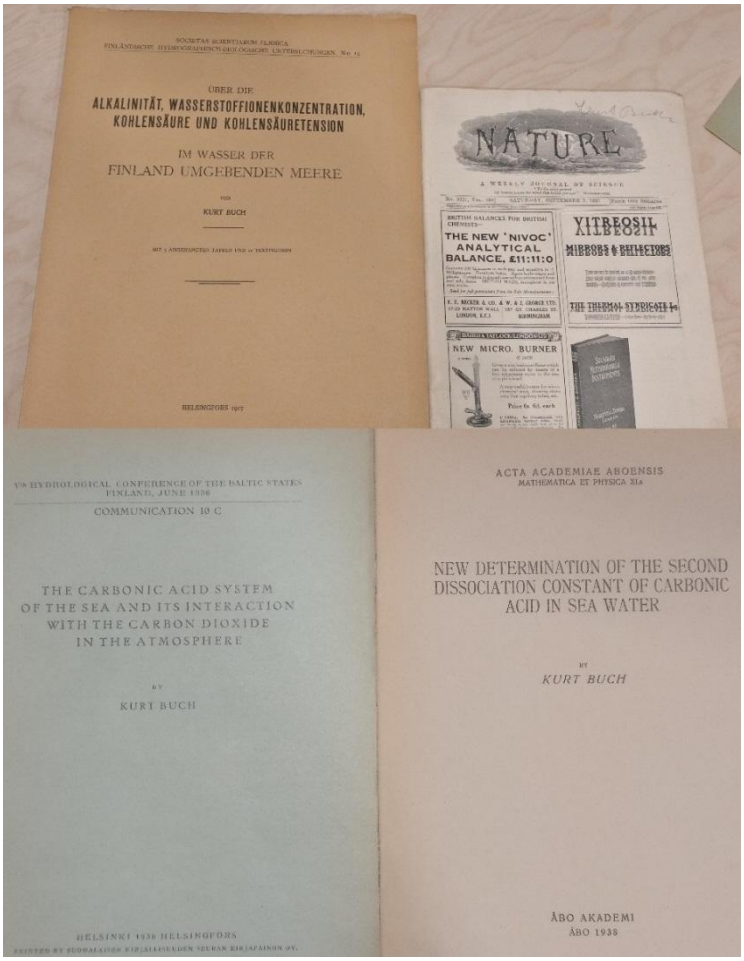

Figure 7. Publications by a marine researcher Kurt Buch.

Alkalinity is dependent on the salinity and consequently the alkalinity in Baltic Sea is much lower than in the oceans. Alkalinity buffers against acidification and therefore pH of Baltic Sea could be lowered more than in the oceans. However, surface water A_T in the Baltic Sea has increased within past two decades which has slowed down the acidification process (Müller et al., 2016). Components of the alkalinity come to the Baltic Sea via rivers. In southern and south-eastern catchment area of the Baltic Sea the soils are rich in limestone and organic matter and rivers transport especially dissolution products of calcium carbonate. In Scandinavia the soils are dominated by siliceous primary rocks and weathering is much slower than in south resulting in lower alkalinity content in northern Baltic Sea.

DIC is produced in and transported to the Baltic Sea. From large catchment of the Baltic Sea rivers transport a lot of allochtonous dissolved organic matter (*DOM*) to coastal waters, which partly mineralizes to *DIC*. Photoproduction of *DIC* from *DOM* increases with decreasing salinity (Aarnos et al., 2012).

Knowledge of the effects of the acidification on the ecosystems in the Baltic Sea is poor, though single species and single factor studies suggest that most species and ecologically significant groups will stay vital with the expected decrease of pH (Havenhand, 2012). Baltic Sea species are probably less sensitive to changes of pH due to naturally large fluctuations in pH compared to more stable acidity conditions in the oceans. Though, eutrophication and increased biological activity may increase fluctuations in the pH seasonal cycle causing increased acidification during net heterotrophic winter time (Omstedt et al., 2010).

3 MATERIALS AND METHODS

3.1 STUDY SITE UTÖ

The experimental data was collected in small, inhabited island Utö (59º 46'50N, 21º 22'23E) in outer archipelago of Finnish coast in northern Baltic proper. Sampling was performed in Atmospheric and Marine Research Station (Figures 8 and 9) which is maintained in collaboration by Finnish Meteorological Institute (FMI) and Finnish Environment Institute. One of the longest records of marine temperature and salinity in the whole Baltic Sea is found from Utö Deep. Observations dates back to 1900. At the moment, Utö belongs to the HELCOM marine monitoring network. Meteorological observations in Utö started in 1881 and atmospheric trace gas and aerosol measurements as member of the EMEP-network in 1980. FMI's atmospheric measurements in Utö Island belong to European ICOS (Integrated Carbon Observation System) network founded in 2008.

Figure 8. Location of the study site Utö. Atmospheric and Marine Research Station is located at A and the inlet of flow-through pumping system at B (NLS MapSite).

Research station completed in 2014 is equipped with flow-through pumping system that draws out water from about 250 meters from the station. The pump (Grundfos MS4000R SP3A-9N) is at the bottom of the sea in 23 meters, but the inlet is kept at 5 meters' depth with floats. The flowrate of the system is from 40 to 50 l/min. Connected to the flow-through pumping system there are various continuously functioning measuring equipment including AFT-pH (Sunburst Sensors) measuring total pH, SuperCO_2 (Sunburst Sensors) measuring partial pressure of CO_2 of the seawater and a thermosalinograph MicroTSG SBE 45 (Sea-Bird Scientific) measuring temperature and salinity.

Figure 9. Atmospheric and Marine Research Station in Utö.

During the measuring campaigns samples were taken 3 times a day at 7am, 1pm and 7pm local time. The campaign dates were: April 4^{th} – 11^{th}, May 4^{th} – 11^{th}, June 28^{th} – July 5^{th} and August 4^{th} – 10^{th} in 2017. Salinity, temperature and pCO_2 data from continuous measurements is used from April 1^{st} to August 31^{st} in 2017.

The sample water was taken from the hose inside the Research Station connected to flow-through pumping system. First the water was let run a while. Alkalinity and *DIC* samples were taken first to their own bottles. Then 4-liter Nalgene-bottle was filled and 50 ml dispenser was attached. Accuracy of the dispenser was checked before use. Date and time of sampling was noted down.

3.2 TOTAL ALKALINITY

Total alkalinity (A_T) was determined by potentiometric titration (Metrohm Titrino 716) (Figure 10). The samples were taken to 0.5 litres plastic bottles with flow-through pumping system in Utö. Samples were conserved with 100 µl of mercury chloride ($HgCl_2$). Due to long duration of measurement, only one sample per sampling time was taken, except two times when three replicates were taken to see the variation of the measurements. Total alkalinity measurements were performed at Finnish Environment Institute's Marine Research Laboratory in Kumpula. The samples were kept cool from 5 to 80 days before the measurements.

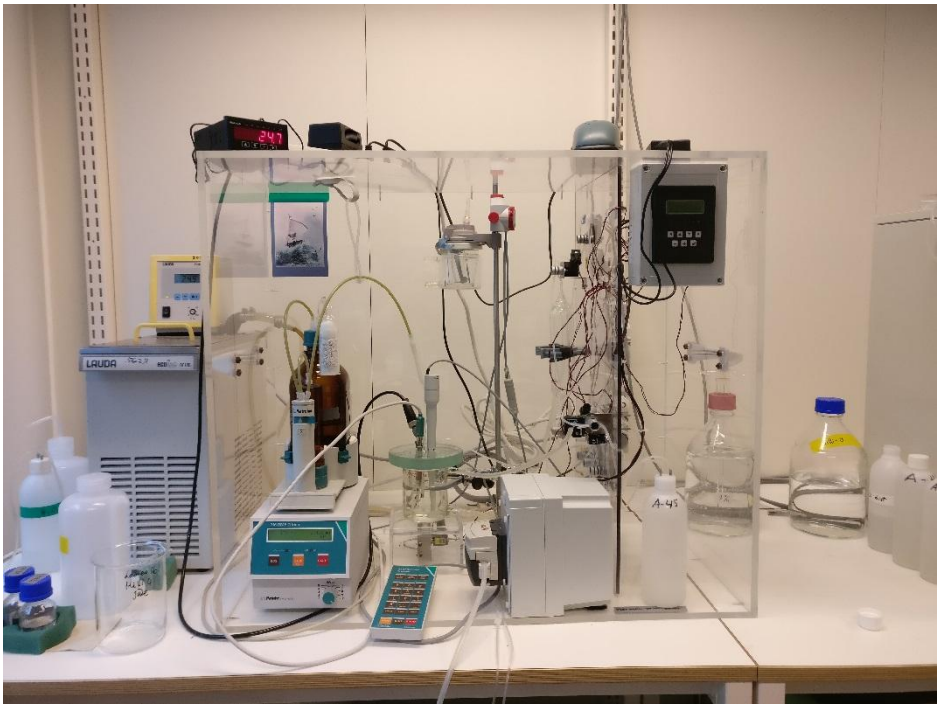

Figure 10. Measurement equipment for total alkalinity.

Before titration the glass pH electrode (Metrohm) was calibrated with pH 4.01 (potassium hydrogen phthalate, Merck Certipur) and pH 9.00 (boric acid/ potassium chloride/ sodium hydroxide solution, Merck Certipur) buffer solutions daily. Performance of the alkalinity measuring system was checked every day with reference sample. Finnish Environment Institute's sea water sample from an open water station LL12 in Gulf of Finland served as

a reference. The apparatus was equipped with automatic rinsing system, which was used between the measurements. For rinsing the equipment salt water solution of salinity 7 was used to minimize changes of salinity for the sensitive pH electrode. Also, the titrant was made into salinity 7 salt water solution. Reaction chamber was kept at 25° C with thermostatic water bath during the titration.

Change of electrode potential in consequence of addition of titrant (0.05 M HCl) to the seawater sample was observed and the titration curve was recorded on computer (QuickBasic compiler and TitraB/Vindta software). Electrode potential increases strongly at two equivalent points: carbonate-bicarbonate and bicarbonate-carbon dioxide equilibriums. Total alkalinity was calculated from the titration curve by Gran method (Gran, 1952) and ordinary least squares method using initial values from Gran method.

3.3 DISSOLVED INORGANIC CARBON

Dissolved inorganic carbon (*DIC*) was measured with Dissolved Inorganic Carbon Analyzer AS-C3 (Apollo SciTech) in Utö (Figure 11). One sample per sampling time was taken with flow-through pumping system to a glass flask with glass stopper. The flask was overfilled with sample to leave the sample without any excess air. Samples were stored in cold (6 °C) when not measured immediately. Samples were kept in cold water bath during the measurements. All the day's samples were measured during the evening sampling.

The analyzer adds 6% phosphoric acid (H_3PO_4) to the sample to convert all the *DIC* species to carbon dioxide (CO_2).

$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3 \quad (16)$$

$$HCO_3^- + H^+ \rightarrow H_2CO_3 \quad (17)$$

$$H_2CO_3 \leftrightarrow H_2O + CO_2 \quad (18)$$

Figure 11. Measurement equipment for dissolved inorganic carbon (Sami Kielosto 2018).

The analyser uses pure nitrogen (N_2) as a carrier gas to move purged CO_2 through a drying system. Li-Cor LI-7000 infrared gas analyser then measures the concentration of dried CO_2 gas.

Three standards were measured first. Weighed amounts (5–15 mg) of sodium carbonate (Na_2CO_3) were dissolved in 100 ml of Milli-Q water. The standard solutions were analysed immediately starting with the lowest sodium carbonate content. Three known *DIC* contents and their relation to measured integrated area under the concentration-time curve were used to form a linear equation. *DIC* contents of the samples were calculated with the equation.

Samples were measured after the standards. The first measurement of each sample (including standards) was discarded since the tubing system must be flushed completely with the sample to get an accurate peak area and avoid carryover effect. Otherwise, the previous measured sample may influence the result. Average of three accepted replicate measurements were calculated from each sample. Analyzer has a Batch-process which automatically discards the first measurement and out of bounds measurements. Batch-process was put into operation by measuring campaign of August. Analyzer was set to measure the sample in 40 seconds after previous measurement and the allowed difference

was 0.1%. The repeatability by the manufacturer is ±0.1% at *DIC* concentrations around 2,000 µmol/L.

Preservability of the samples was tested by taking three replicate samples with two evening sampling times. One replicate was measured immediately and another ones the next morning.

3.4 SEAWATER PH

Seawater pH is measured continuously in Utö Atmospheric and Marine Research Station with AFT-pH (Autonomous Flow-Thru) instrument (Sunburst Sensors) (Figure 12). This spectrophotometric pH measurement uses pH-dependent indicator meta-Cresol Purple (mCP) as a reagent. Two LEDs send light pulses through the reagent-sample mixture at wavelengths corresponding maximum optical absorbance for the protonated and deprotonated forms of the reagent (434 nm and 578 nm). Indicator dye changes colour according to sample pH and the colour affects absorbance spectra of the reagent. Measured absorbances and the known molar absorptivities of the reagent are used to determine pH of the sample based on Beer's law.

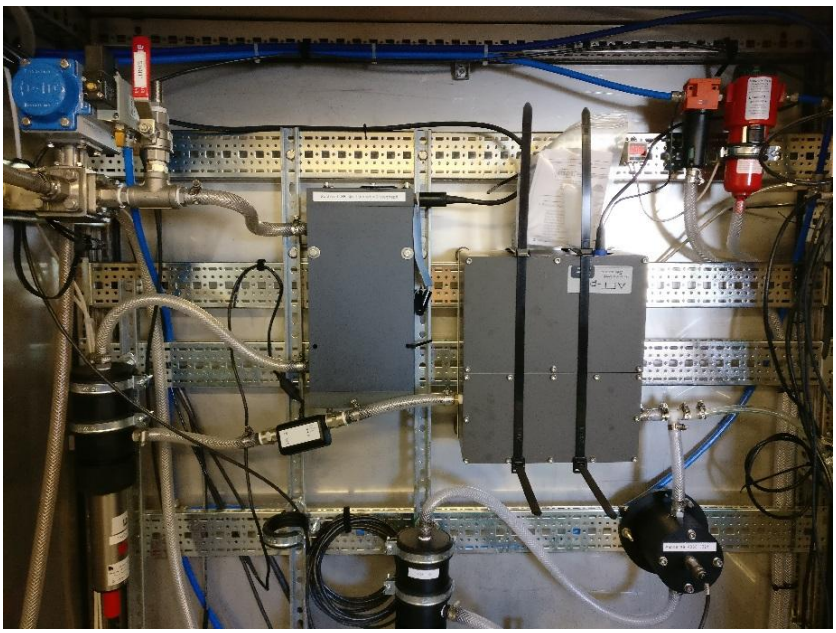

Figure 12. Measurement equipment for pH connected to flow-through pumping system

Dye's molar absorptivities and dissociation constant are dependent on temperature and sample water's salinity and the dye must be characterized for the temperature and salinity range where it is used. AFT-pH instrument measures temperature of the sample but the salinity correction was done afterwards with executable QC_PH_02lowS provided by Sunburst Sensors to get accurate values for low salinities. The measured values are pH values in total hydrogen ion scale. AFT-pH instrument is automatically cleaned daily by Triton-X detergent.

3.5 PARTIAL PRESSURE OF CO_2

Partial pressure of CO_2 is also measured continuously in Utö Atmospheric and Marine Research Station with SuperCO_2 instrument (Sunburst Sensors) and two showerhead equilibration chambers (Figure 13). CO_2 is equilibrated between the sample water and air in the equilibration chambers. Air is then directed to LI-840a gas analyser (Li-cor). The equipment is calibrated every four hours with four calibration gases which have following CO_2 contents: 0.0, 234.38, 396.69, 993.45. Raw data from the SuperCO_2 was corrected by a Python script that takes into account the calibration measurements and removes data from maintenance and automatic clean-up periods. Equilibration chamber is cleaned daily automatically with hydrogen peroxide.

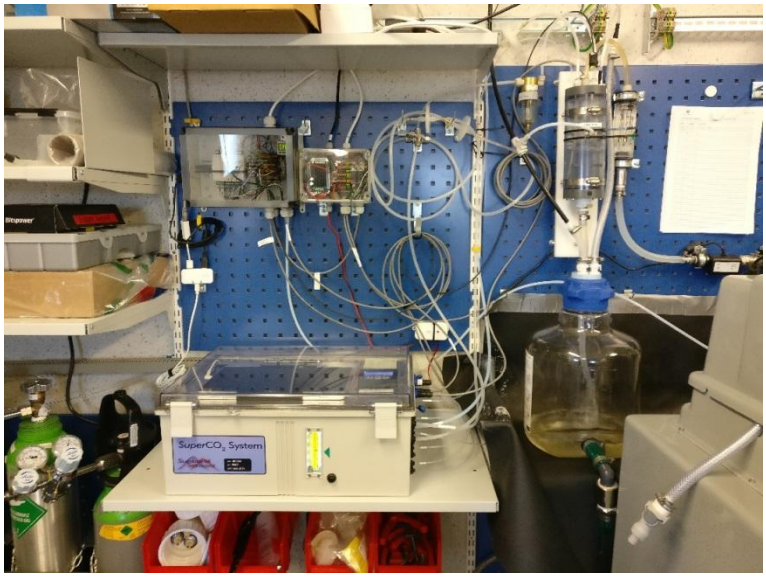

Figure 13. Measurement equipment for pCO_2 connected to the flow-through pumping system.

3.6 INORGANIC CARBON SYSTEM MODELLING

CO_2 system calculations and modelling were performed with CO2calc software (Robbins et al., 2010) (Figure 14). To start with, the software is designed for conditions in oceans. There are a lot of options for different constants to choose from. In this study Millero's (2010) carbonate constants (K_1 and K_2) for estuarine waters were chosen for Baltic Sea's low salinity conditions (Table 1). For dissociation constant of bisulphate K_{SO4} was chosen values from Dickson (1990) and total boron was calculated from salinity based on measurements by Lee et al. (2010). Among other constants applied by the software were K_W from Millero (1995), K_0 from Weiss (1974) and K_F from Perez & Fraga (1987). Also, user must choose between four different pH scales (free, total, seawater and NBS). Our pH measuring instrument gives results in total scale and so that was used in the calculations. Choices for air-sea flux and wind speed units did not signify because air-sea CO_2 fluxes were not considered in this work.

Table 1. Options chosen for CO2calc software calculations. Dissociation constant values depend on salinity and temperature. Total boron is estimated by the ratio of boron to chlorinity.

Parameter	Choice
Dissociation constant for H_2CO_3* K_1	Millero (2010)
Dissociation constant for HCO_3^- K_2	Millero (2010)
Dissociation constant for HSO_4 K_{SO4}	Dickson (1990)
Boron total	Lee et al. (2010)
pH scale	Total scale

A_T, *DIC*, pH and pCO_2 were all modelled with all the combinations of two other measurable components of carbonate system. Measured values from two inorganic carbon system components together with salinity and temperature values as well as sample depth (5 m) were put down in an excel sheet. Amounts of phosphorus and silicon were not used. CO2calc software then calculated concentrations of the other components. CO2calc is based on carbonate system model (equations 5, 12–15). Alkalinity, however, is simplified in the following form (Robbins et al., 2010):

$$A_T = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] - [H^+]_F - [HF] - [HSO_4^-] - [H_3PO_4] \quad (19)$$

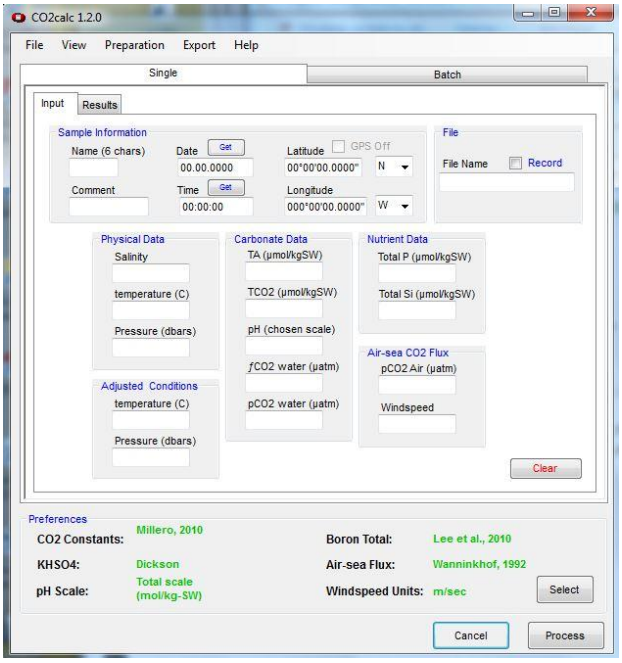

Figure 14. View from CO2calc software window (Robbins et al., 2010).

3.7 DATA PROCESSING AND STATISTICAL METHODS

Temperature and salinity raw data contains values at intervals of 15 seconds. The periods of maintenance and automatic clean-ups were removed from the time series. Average values for temperature and salinity were calculated from the values ± 1 minute from the measurement times.

A_T was determined from the titration curve by two different methods: Gran method (Gran 1952) and ordinary least squares method using initial values from Gran method. Both results are presented. Standard deviation and coefficient of variation *CV* were calculated from the replicate samples to estimate the precision of the measurement. The alkalinity of the seawater sample that was measured for reference is not known. Reference sample measurements were thus used for precision estimation and the accuracy of the measurements is unclear.

Every *DIC* sample was measured repeatedly to get at least three accepted replicate measurements. Repetitions were made manually, except at measuring campaign of August, when Analyzer's Batch-process was put into operation. Batch-process automatically discards the first measurement and out of bounds measurements. The *CV* limit for the Batch process was 0.1 %. From earlier campaigns the out of bounds measurements were discarded if *CV* was larger than 0.2 %. Average of the accepted values was used as a sample's *DIC* result. The standard solutions had more variation in replicate measurements and only a few times *CV* was under 0.2 %. Therefore, no measurements were discarded, and the median was used as a result. *CV* of the three replicate samples was calculated to get the variation caused by preservation.

Continuous pH measurement equipment takes measurements every 15 minutes. The periods of maintenance and automatic clean-ups were removed from the data as well as obvious outliers. Data had to be corrected by QC_PH_02lowS with real salinity values. For every campaign the average salinity of the period was used. Temporally closest pH value was used for every campaign measurement time. Also, median values for every hour were calculated for the campaign periods.

Continuous pCO_2 is measured at intervals of 10 seconds. Periods of calibration, maintenance and automatic clean-ups were removed with a python script wrote by Honkanen (2017). Raw data was corrected by the calibration data. Average of pCO_2 values from time of measurement ± 2 minutes was used for every campaign measurement time. Hourly median values were calculated for the campaign periods.

Hourly median values from Finnish Meteorological Institute were used for the whole summer figures of temperature, salinity and pCO_2. Periods of maintenance and automatic clean-ups were removed.

Spearman correlations were calculated for A_T, *DIC*, pH, pCO_2, temperature and salinity. The choice of Spearman's rank correlations instead of Pearson correlations was made because of nonlinear relationships of the components. Correlations with A_T and/or *DIC* were calculated from data containing only campaign measurement times. Other correlations were calculated with hourly median values from the campaign weeks as well as linear regressions were calculated for alkalinity and DIC using salinity and temperature as explanatory variables. Calculations were performed with RStudio (Version 1.0.153).

The results of the modelled parameters were compared to measured values with error analysis. Random error was estimated by Root Mean Square Error RMSE (Equation 20). Systematic error was estimated by Bias B (Equation 21). Mean percentage error MPE was also calculated (Equation 22).

$$RMSE = \left[\frac{1}{N-1}\sum_{i=1}^{N}(P_i - O_i)^2\right]^{1/2} \tag{20}$$

$$B = \frac{1}{N}\left(\sum_{i=1}^{N} P_i - \sum_{i=1}^{N} O_i\right) \tag{21}$$

$$MPE = 100\frac{1}{N}\sum_{i=1}^{N}\left|\frac{P_i - O_i}{O_i}\right| \tag{22}$$

In equations P means predicted value that is modelled value and O is observed or measured value.

4 RESULTS

4.1 SUMMER 2017

In 2017 temperature of surface water in Utö rose steadily from 2° C in April to 16° C in the end of July. In August the temperature stayed between 12.5-16° C. Salinity was at highest level in April and May being most of the time between 6.6 and 6.7. In June and July salinity declined to almost 6. In August salinity was 6.2–6.3. From April to August partial pressure of CO_2 was below the atmospheric content, which varied between 390 and 420 ppm in 2017 in Utö (Finnish Meteorological Institute, 2018). Lowest values of pCO_2 (minimum 213 ppm in May) were not reached during the measurement campaigns. In late August seawater pCO_2 rose above atmospheric content of CO_2.

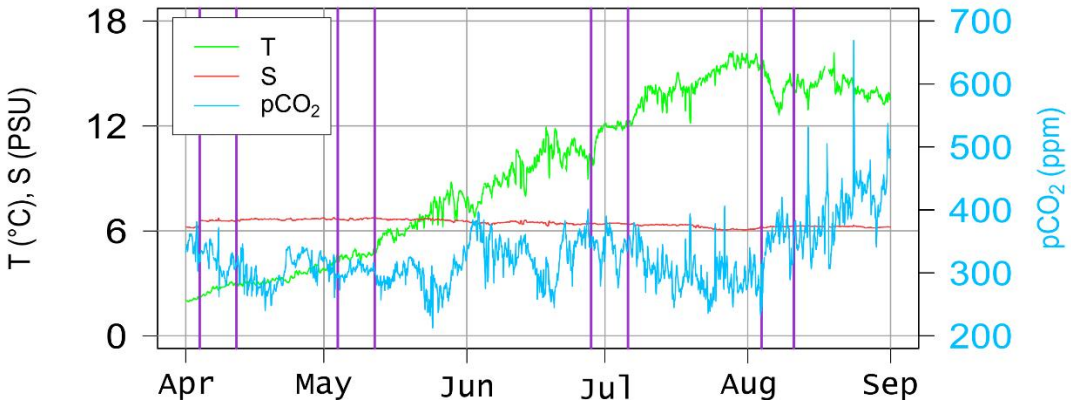

Figure 15. Temperature (green line), salinity (red line) and partial pressure of CO_2 (blue line) in water at Utö in summer 2017. Purple vertical lines indicate four periods of measurements 4.–11.4., 4.–11.5., 28.6.–5.7. and 4.–10.8.2017. Note the different scale in the right side for the partial pressure of CO_2.

4.2 MEASUREMENT CAMPAIGNS

Seawater samples were taken during four one-week-long measurement campaigns in spring and summer in 2017 (Figure 17). Both A_T and *DIC* were in their highest level during April and May measurement campaigns. A_{Gran} maximum was 1630 µmol kg^{-1} and A_{OLS} maximum was 1610 µmol kg^{-1} in May, while *DIC* was measured 1560 µmol kg^{-1}. Both A_T

and *DIC* declined to the June-July campaign and even further in the August along with salinity decline. Both A_T and *DIC* are strongly correlated with salinity (Table 2, Figure 18). The two alkalinity values A_{Gran} and A_{OLS} correlate tightly (R=0.965, p<0.001), but they differ from each other on average about 30 µmol kg^{-1} (about 2%).

CV calculated from two sets of three replicate alkalinity samples was 0.3-0.4%. *CV* for A_{Gran} was slightly smaller than for A_{OLS}. Variation caused by preservation of *DIC* samples was estimated with two sets of samples in which one sample was measured right away and two samples were conserved overnight. Calculated *CV* was 0.4%.

Finnish Environment Institute's sea water sample from an open water station LL12 in Gulf of Finland was used as a reference sample for precision estimation. Alkalinity of the reference sample was determined before measurements every day. There is a drop of roughly 30 µmol kg^{-1} between reference alkalinity results in May and June (Figure 16). Results were not corrected due to the change, because the cause of the change is not known. Either something has happened to the reference sample or the change has occurred in the measurement equipment.

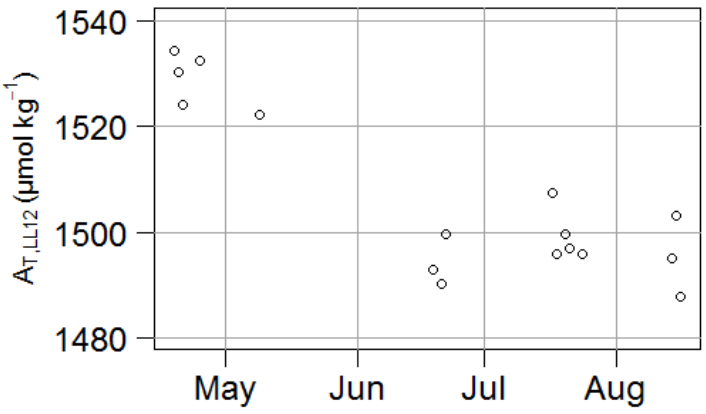

Figure 16. Reference sample LL12 for alkalinity

Diagrams of pH and pCO_2 are mirror images of each other: spikes in pH curve correspond to lows in pCO_2 curve and vice versa (R=-0.941, p<0.001) (Figure 17). Values of pH stay between 8.0 and 8.3 in all the campaigns. In measurement week in May pH and pCO_2 are

quite stable, whereas during other campaigns the variation is larger. During all the measurement campaigns pCO_2 stays under atmospheric CO_2 level 390–420 ppm (Finnish Meteorological Institute, 2018) except for one spike in August. At lowest pCO_2 was during campaign in August 264 ppm. After the last measurement campaign pCO_2 content rose above atmospheric CO_2 level (Figure 16).

The two alkalinity values A_{Gran} and A_{OLS} was found to correlate tightly (R=0.965, p<0.001) (Table 2, Figure 18). There was also strong correlation between alkalinity and salinity (R=0.951, p<0.001 and R=0.901, p<0.001). *DIC* correlated with salinity (R=0.933, p<0.001) and alkalinity (R=0.893, p<0.001 and R=0.859, p<0.001). For temperature, correlation coefficients with A_{OLS}, $A_{Gran,}$ *DIC* and salinity were -0.86, -0.79, -0.76 and -0.75 respectively coefficient of determination R^2 being between 0.56 and 0.74. Linear regression with temperature and salinity as explanatory variables for alkalinity and DIC gives adjusted R^2 0.89-0.92. Only in A_{OLS} model temperature component is significant. Continuous measurements pH and pCO_2 had a strong negative correlation (R=-0.941, p<0.001), but with other components the maximum absolute value of correlation coefficient is 0.62. Due to large data set all the calculated correlation coefficients are statistically significant.

Table 2. Spearman correlation coefficients R for inorganic carbon system variables

	A_{OLS}	A_{GRAN}	DIC	pH	pCO2	Temp.
A_{OLS}	1					
A_{GRAN}	0.965***	1				
DIC	0.859***	0.893***	1			
pH	0.462***	0.501***	0.482***	1		
pCO2	-0.542***	0.589***	-0.552***	-0.941***	1	
Temperature	-0.860***	-0.759***	-0.759***	-0.331***	0.435***	1
Salinity	0.901***	0.951***	0.933***	0.573***	-0.616***	-0.745***

Level of significance *** p < 0,001 ** p < 0,01 *p < 0,05

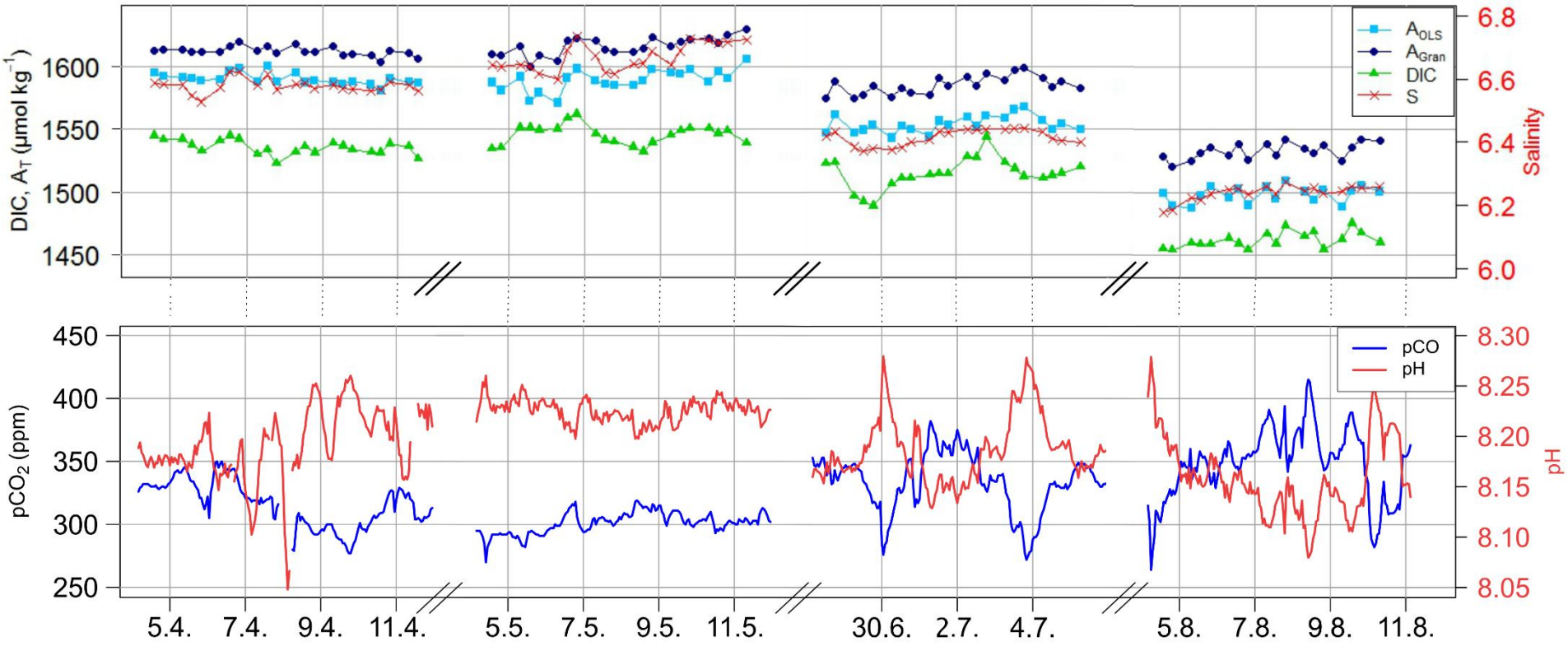

Figure 17. Inorganic Carbon System in Utö during four measurement campaigns in 2017. Gran method (blue diamonds) and ordinary least square - method (light blue squares) of alkalinity, dissolved inorganic carbon (green triangles) and salinity (red x-marks) are shown in the upper diagram. Down are pH (red) and pCO_2 (blue). Note the scales for salinity and pH in the right side.

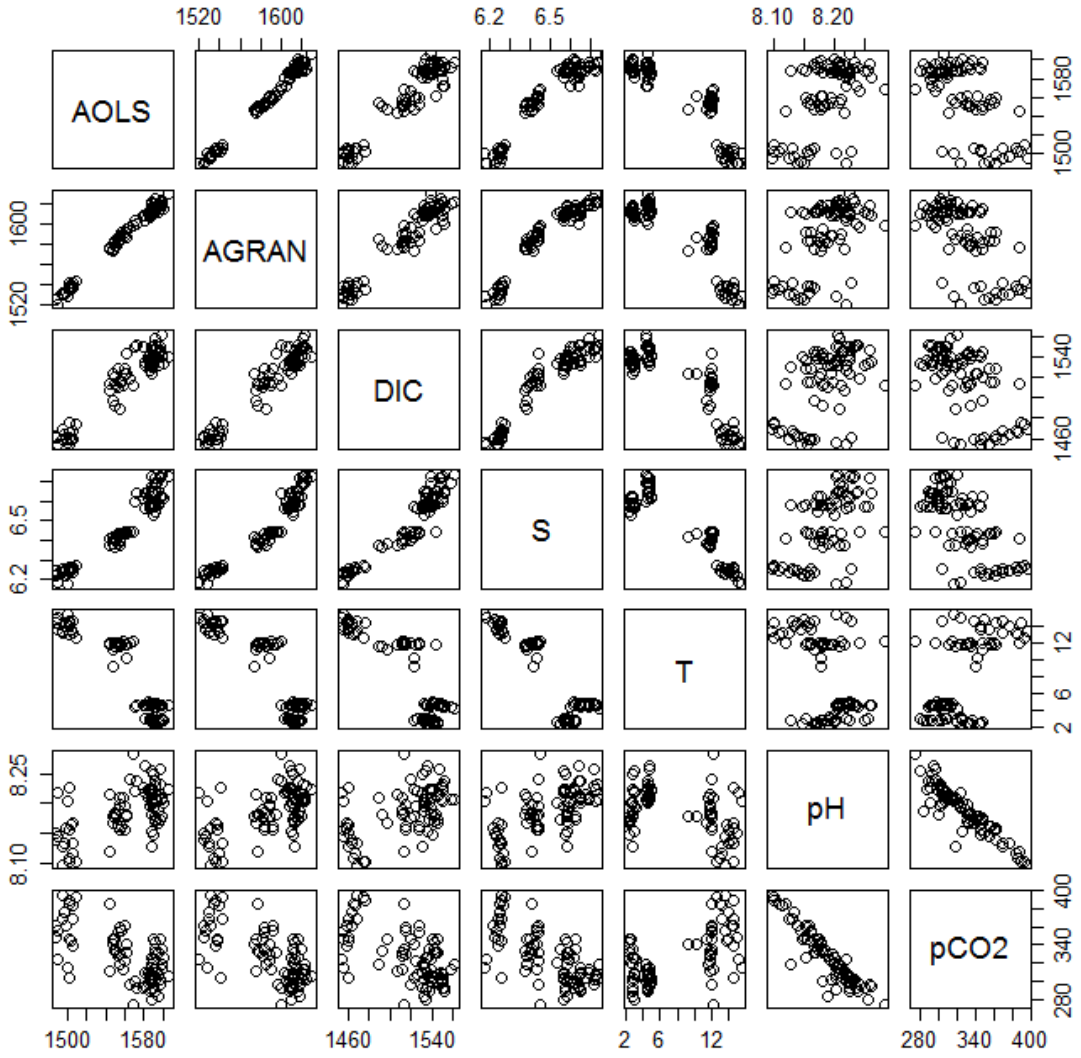

Figure 18. Diagrams of correlations between different components of inorganic carbon system

4.3 MODELLING

Carbonate system modelling were performed with CO2calc software (Robbins et al., 2010). A_T, *DIC*, pH and pCO_2 were all modelled with all the combinations of two other measurable components of carbonate system. Correlations between A_T and *DIC* and between pH and pCO_2 was seen also in modelling results. Alkalinity modelled by pH and pCO_2 had large systematic (B > 220 µmol kg^{-1}) and random errors (RMSE > 230 µmol kg^{-1}) and MPE was 14–16 % compared to measured A_{Gran} and A_{OLS} values (Figure 19, Table 3). When modelling included measured *DIC* values, bias was between -3 and -41 µmol kg^{-1}, RMSE was between 17 and 44 µmol kg^{-1} and MPE was under 2.6 %. Modelling results were slightly better with measured pH than with measured pCO_2. In any case, MPEs for modelled results are larger than calculated *CV* for alkalinity (0.3-0.4%).

Modelling *DIC* by pH and pCO_2 resulted also in large systematic (B = 250 µmol kg^{-1}) and random errors (RMSE = 260 µmol kg^{-1}) and MPE was 16 % compared to measured *DIC* values (Figure 20, Table 4). Modelling *DIC* with A_T as one measured component improved modelling results. Bias was then between 3 and 40 µmol kg^{-1}, RMSE between 17 and 40 µmol kg^{-1} and MPE was under 2.6 %. Modelling DIC with measured pH instead of measured pCO_2 resulted in somewhat better results. Also, using A_{OLS} instead of A_{Gran} gave a bit better results. However, even the smallest MPE from modelling DIC with pH and A_{OLS} (0.93%) is larger than variation caused by preservation of *DIC* samples (*CV* 0.4%).

Due to strong correlation between pH and pCO_2 modelling these parameters gave better results when the other one was used in modelling (Figures 21 and 22, Tables 5 and 6). Results were very similar with each other irrespective of whether the second measured component was A_{Gran}, A_{OLS} or *DIC*. However, there is a difference between the modelling results and measured values. Bias ranged from -0.054 to -0.065 for pH and from -40 to -45 ppm for pCO_2. Bias and RMSE were larger when the modelling was based on A_T and *DIC* values.

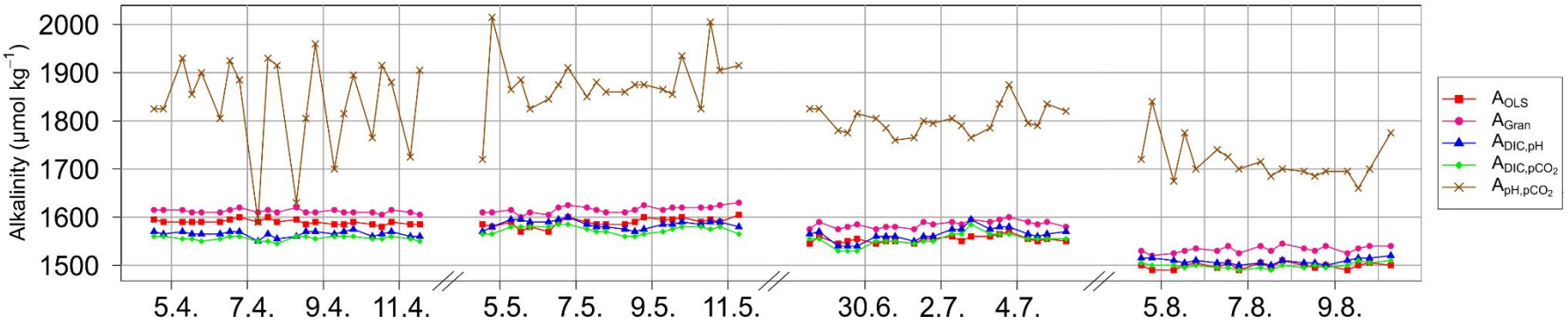

Figure 19. Results of measured (red and pink) and modelled total alkalinity in Utö during the measuring campaigns in 2017. Blue triangles indicate A_T modelled by *DIC* and pH measurements, green diamonds by *DIC* and pCO_2 measurements and brown x-marks by pH and pCO_2 measurements.

Table 3. Results from the error analysis for modelled alkalinity

Measured	Modelled by	RMSE (µmol kg^{-1})	Bias (µmol kg^{-1})	MPE
AOLS	pH, pCO2	261.63	250.89	16.06 %
AOLS	DIC, pH	17.39	-3.06	0.92 %
AOLS	DIC, pCO2	21.73	-13.10	1.07 %
AGRAN	pH, pCO2	234.68	222.52	14.02 %
AGRAN	DIC, pH	34.25	-31.43	1.97 %
AGRAN	DIC, pCO2	43.74	-41.47	2.60 %

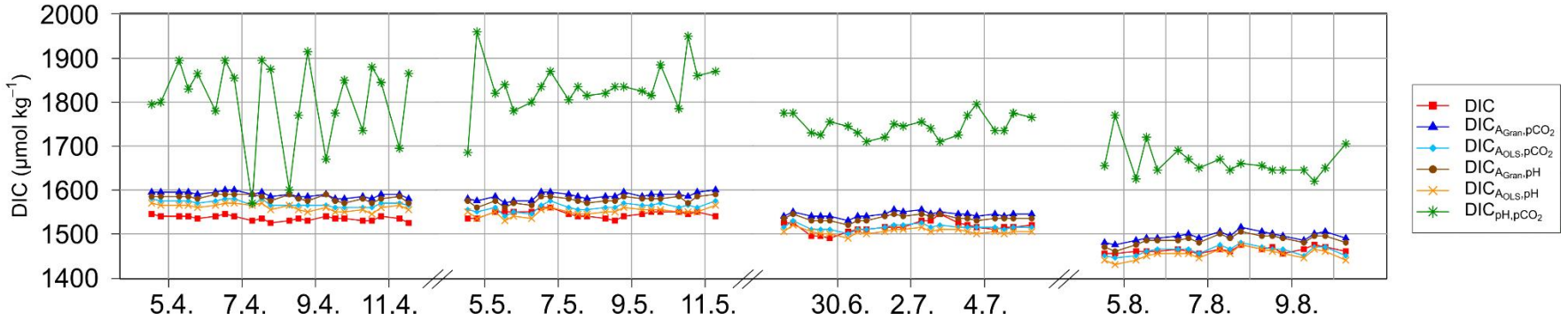

Figure 20. Results of measured (red squares) and modelled dissolved inorganic carbon in Utö during the measuring campaigns in 2017. Blue triangles indicate *DIC* modelled by A_{Gran} and pCO_2 measurements, light blue diamonds by A_{OLS} and pCO_2 measurements, brown circles by A_{Gran} and pH measurements, yellow x-marks by A_{OLS} and pH measurements and green stars by pH and pCO_2 measurements.

Table 4. Results from the error analysis for modelled *DIC*

Measured	Modelled by	RMSE (µmol kg^{-1})	Bias (µmol kg^{-1})	MPE
DIC	pH, pCO2	259.86	248.97	16.38 %
DIC	AGRAN, pCO2	41.50	39.29	2.59 %
DIC	AGRAN, pH	33.68	30.87	2.03 %
DIC	AOLS, pCO2	20.70	12.49	1.05 %
DIC	AOLS, pH	17.09	3.07	0.93 %

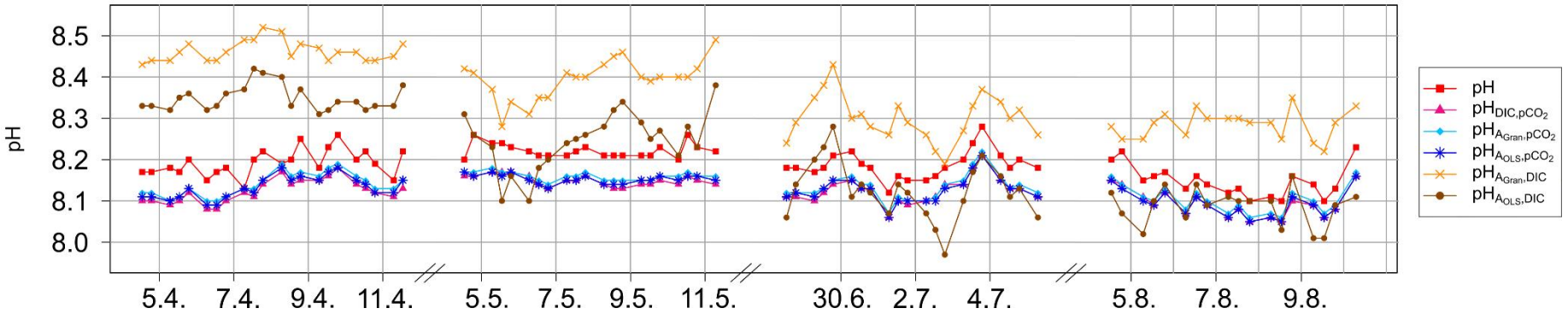

Figure 21. Results of measured (red squares) and modelled pH in Utö during the four measuring campaigns in 2017. Pink triangles indicate pH modelled by *DIC* and pCO_2 measurements, light blue diamonds by A_{Gran} and pCO_2 measurements, blue stars by A_{OLS} and pCO_2 measurements, yellow x-marks by A_{Gran} and *DIC* measurements and brown circles by A_{OLS} and *DIC* measurements.

Table 5. Results from the error analysis for modelled pH

Measured	Modelled by	RMSE	Bias	MPE
pH	DIC, pCO2	0.0669	-0.0645	0.79 %
pH	AGRAN, DIC	0.1926	0.1757	2.15 %
pH	AGRAN, pCO2	0.0561	-0.0535	0.66 %
pH	AOLS, DIC	0.1075	0.0187	1.08 %
pH	AOLS, pCO2	0.0633	-0.0610	0.74 %

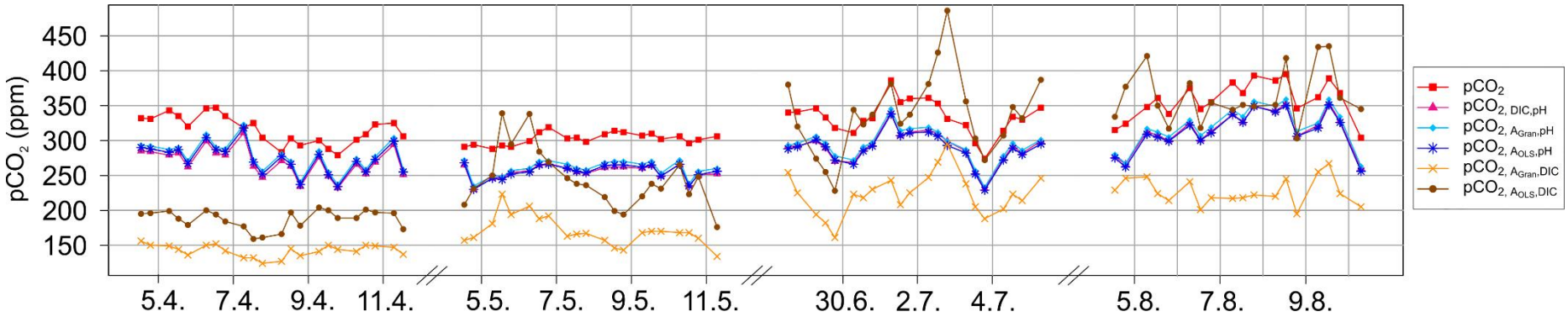

Figure 22. Results of measured (red squares) and modelled pCO_2 in Utö during the measuring campaigns in 2017. Pink triangles indicate pCO_2 modelled by *DIC* and pH measurements, light blue diamonds by A_{Gran} and pH measurements, blue stars by A_{OLS} and pH measurements, yellow x-marks by A_{Gran} and *DIC* measurements and brown circles by A_{OLS} and *DIC* measurements.

Table 6. Results from the error analysis for modelled pCO_2

Measured	Modelled by	RMSE (ppm)	Bias (ppm)	MPE
pCO2	DIC, pH	46.59	-45.26	13.95 %
pCO2	AGRAN, DIC	142.51	-137.50	42.31 %
pCO2	AGRAN, pH	41.14	-39.59	12.24 %
pCO2	AOLS, DIC	83.60	-47.00	21.17 %
pCO2	AOLS, pH	46.21	-44.82	13.79 %

5 DISCUSSION

Summer 2017 was slightly cooler than average summer in Utö. That had an influence on the seawater temperature. During our period of measurement surface temperature stayed under 16° C. According to a data from over 100 years of measurements in Utö, average surface temperature has varied between 0° C during and 18° C during summer (Laakso et al., 2018).

Also salinity has been measured in Utö over 100 years. According these measurements surface salinity has ranged between 6 and 7 and it has a seasonal cycle being lower during summer and higher during winter (Laakso et al., 2018). Freshwater inflow from catchment area is usually greatest in spring as the snow melts. Also, thermal stratification in summer keeps less dense, less saline water at the uppermost layer. Largest river runoffs into the Gulf of Finland come from the Neva River, which corresponds to approximately 70% of the fresh water inflow (Bergström and Carlsson, 1994). Located about 500 km east from Utö Island, inflow from Neva River affect waters in our study site with delay (Ylöstalo et al., 2016). In our dataset salinity was at highest in April and May (under 6.7) and it declined as summer advanced. At lowest salinity had fallen to almost 6 in end of July. Hence our measurements followed the trends observed by Laakso et al. (2018).

5.1 MEASUREMENTS OF INORGANIC CARBON SYSTEM

Carbonate system has been investigated in the Baltic Sea starting a century ago by a marine researcher Kurt Buch (1917, Figure 7). In our measurement campaigns A_{Gran} was at highest 1630 µmol kg^{-1} in May and it declined towards the end of summer being 1520 µmol kg^{-1} at lowest. Measured A_{OLS} values were 1610 and 1490 µmol kg^{-1} respectively. Alkalinity concentration around Utö in 2009 was approximately 1600–1700 µmol kg^{-1} during winter and 1500–1600 µmol kg^{-1} during summer (Beldowski et al., 2010; Joensuu, 2010). Hjalmarsson et al. (2008) have evaluated historical alkalinity data from Baltic Sea. According to them, mean surface water A_T is between 1400 and 1600 µmol kg^{-1} in the waters of northern Baltic proper. Changes in alkalinity or salinity both are related to changes in water bodies and mixing or evaporation and precipitation. Therefore, alkalinity and salinity usually have a linear relationship regionally. Decline of alkalinity during the summer in our measurements followed the changes in salinity as expected.

River runoffs of A_T into the Baltic Sea have been growing over the past century increasing the alkalinity concentration of the seawater (Hjalmarsson et al., 2008; Müller et al., 2016). Müller et al. (2016) suspect the reasons for increased A_T are increasing atmospheric pCO_2, liming activities and acidic precipitation in southern part of the Baltic Sea drainage basin. The bedrocks of the southern and northern catchment areas differ from each other. In north, bedrock is mostly granite and there's only a thin layer of soil whereas in south the bedrock consists mainly of limestone, clay and sandstone covered with thick layer of soil. These differences in bedrocks affect the weathering processes and therefore the impacts of the acidic rains are different in northern and southern catchment areas. Peak in acidic precipitations was in 1980s, but atmospheric pCO_2 is still rising steadily. Increasing CO_2 contents has a direct and an indirect effect on terrestrial weathering. Indirect effect means excess CO_2 is stimulating plant growth and soil respiration raising soil pCO_2, which affects mineral weathering. Alkalinity rise mitigates the acidification due to increasing atmospheric pCO_2.

The trend in our *DIC* measurements was also descending during the summer. Alkalinity and *DIC* have the same main components, bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}). Therefore, concentrations of *DIC* and alkalinity are usually correlated and in our measurements *DIC* did follow the changes in alkalinity. In May *DIC* concentration reached 1560 µmol kg^{-1} and in August the concentration was 1455 µmol kg^{-1}. Our results are very similar compared to the earlier studies in our study area in Baltic Sea. Thomas and Schneider (1999) measured *DIC* in summer 1994 (1300–1400 µmol kg^{-1}) and in winter 1995 (1500–1600 µmol kg^{-1}). Beldowski et al. (2010) measured *DIC* on a cruise in summer 2008 and in northern Baltic proper it was 1400–1550 µmol kg^{-1}. During winter 2009 *DIC* was approximately 1600 µmol kg^{-1} and in the summer 1400 µmol kg^{-1} (Joensuu, 2010).

Large seasonal variations in biological activity in Baltic Sea results in very large fluctuations in pCO_2 (100–1100 ppm) and pH (6.4–9.4) (Omstedt et al., 2010; Saderne et al., 2013; Schneider, 2011; Schneider and Müller, 2018). There is a clear seasonal cycle observed (e.g. Thomas & Schneider 1999). During summer time, biological CO_2 uptake for primary production decreases pCO_2 and increases pH. In winter, respiration and decomposition increase pCO_2 above atmospheric level. In our measurements pCO_2 does not get below 200 ppm and during measurement campaigns the minimum is 264 ppm. Seawater pCO_2 stays under atmospheric CO_2 level (390–420 ppm) during the summer until the mid-August. In other words, seawater ecosystem is net autotrophic until the end of

summer. Seawater pH varies between 8.0 and 8.3 during the campaigns. Seawater pH and pCO_2 show clear inverse correlation as expected ($R=-0.941$, $p<0.001$). CO_2 dissolves in water and forms carbonates (Equations 13–15). Content of pCO_2 has a direct link to a content of hydrogen ions (H^+) which determines pH of the water (Equation 12).

In this study alkalinity is strongly correlated with salinity ($R=0.951$, $p<0.001$) (Table 2, Figure 18), which supports previous studies in Baltic Sea (Hjalmarsson et al., 2008; Müller et al., 2016). The only exception in Baltic Sea is Gulf of Riga where alkalinity and salinity has been shown to have a negative correlation due to limestone-rich soils of the catchment area of River Daugava (Beldowski et al., 2010; Hjalmarsson et al., 2008). Also, *DIC* correlated with salinity ($R=0.933$, $p<0.001$) and there was a relation between *DIC* and alkalinity too ($R=0.893$, $p<0.001$) like earlier studies in Baltic Sea has shown (Joensuu, 2010; Thomas and Schneider, 1999). Salinity declined during the summer while seawater temperature rose quite steadily. Correlation coefficient between temperature and salinity was -0.75. Correlation coefficients between temperature and A_{Gran} or *DIC* were on the same level (-0.79 and -0.76 respectively). Perhaps strong correlation with salinity leads to that A_{Gran} and *DIC* seem to have a fair correlation with temperature.

5.2 MEASUREMENT TECHNOLOGY AND UNCERTAINTIES

Sampling water was taken from about 250 meters from the research station. The inlet is kept at 5 meters' depth, but the pump and the pipe are at the bottom of the sea in 23 meters. In summer, temperature difference between water in 5 m and at the bottom may be great. It is therefore possible that water taken from 5 m cools down moving along the pipe at the bottom. That may affect especially pCO_2 values and also pH values. Time from inlet to the research station is about 7 to 9 minutes when flowrate of the system is from 40 to 50 l/min.

With *DIC* measurements, large variation in standard solution measurements is probably caused by heterogeneous dissolving of sodium carbonate (Na_2CO_3). Uncertainty in standard measurements affects the accuracy of the *DIC* results. Therefore, some tests examining sodium carbonate dissolution might be in order.

Total alkalinity was determined from the titration curve by two different methods: Gran method (Gran, 1952) and ordinary least squares method using initial values from Gran method. Results of these two methods correlate tightly ($R=0.965$, $p<0.001$), but they differ from each other A_{Gran} being about 30 µmol kg^{-1} higher. The true alkalinity of the seawater sample LL12 that was measured for reference is not known. It would be good to check the

accuracy of the alkalinity measurements with a certified reference material. That would make it easier to make the choice between the two methods for calculating the alkalinity value from the titration curve. Drop in reference alkalinity results between May and June samplings (Figure 16) raises questions: has something happened to the reference sample or is the change occurred in the measurement equipment? Furthermore, glass pH electrode did not meet the requirements of pH=7+-0.20 and slope 98–102% every time when calibrated with buffer solutions. That may indicate that deteriorated functioning of the pH electrode might be the reason behind the change in reference alkalinity results.

5.3 MODELLING

Modelling carbonate system with CO2calc software (Robbins et al., 2010) gave better results when modelling was performed with one of the pair A_T and *DIC* combined with pH or pCO_2. Choice for dissociation constants of carbonic acid (K_1 and K_2) has a great influence on the results, whereas other options like K_{SO4} and total boron calculation method have an effect of under 0.02%. The effect of K_1 and K_2 on the results is largest when the seawater salinity low like in Baltic Sea and may be several percentage points.

Best results for alkalinity were obtained with *DIC* and pH measurements. Compared to measured A_{OLS} values bias was -3 µmol kg^{-1} and RMSE was 17 µmol kg^{-1} and MPE was 0.9 %. *CV* of the A_{OLS} measurements was 0.4 %. Comparing to A_{Gran} measurements the modelling results were slightly worse MPE being at best 2.0 %. *DIC* modelling by A_{OLS} and pH fits best the measurement results (B = 3 µmol kg^{-1}, RMSE = 17 µmol kg^{-1}, MPE = 0.9 %). The repeatability of *DIC* measurements reported by the manufacturer is ±0.1 % with *DIC* values around 2000 µmol kg^{-1} which means precision of 2 µmol kg^{-1}. Preservation of the samples causes CV of 0.4 %. When alkalinity or *DIC* was modelled by the continuous measurements pH and pCO_2 the results were much too large. Bias was larger than 220 µmol kg^{-1}, RMSE larger than 230 µmol kg^{-1} and MPE was 14–16 %. Another one of the pair A_T and *DIC* should therefore be used when modelling the other one. Using A_{OLS} values instead of A_{Gran} values gave better results when modelling *DIC*, but we cannot know if A_{OLS} values represents true values of A_T better than A_{Gran} values.

Modelling of pH and pCO_2 with discrete measurements A_T and *DIC* resulted in large RMSE (for pCO_2 80–140 ppm, for pH 0.11–0.19), bias (for pCO_2 50–140 ppm negative, for pH 0.02–0.18) and MPE (for pCO_2 21–42 %, for pH 1.1–2.2 %). Results were better when modelling with another continuous measurement. The other modelling component

A_{Gran}, A_{OLS} or *DIC* hardly affected the results. However, modelling results with another continuous measurement were systematically too low compared to measured values. Bias ranged from -0.054 to -0.065 for pH and from -40 to -45 ppm for pCO_2 and MPE was 0.66–0.79 % and 12–14 % respectively. Kuliński et al. (2014) measured carbonate system components from 19 sampling stations in Baltic Sea. They calculated pH and pCO_2 with CO2SYS (forerunner of CO2calc) by measured A_T and *DIC* and also by measured A_T and pH or pCO_2. They used dissociation constants of carbonic acid developed by Millero et al. (2006). We used newer constants by Millero (2010) which are updated from the earlier constants (Millero et al., 2006) and those are very close to each other. Both in our and in calculations of Kuliński et al. (2014) K_{SO4} was applied according to Dickson (1990). Calculations with A_T and *DIC* resulted in large discrepancies like in our measurements. Calculations with A_T and pCO_2 were 10–47 µatm higher than measured values whereas in this study the calculations underestimated pCO_2. Also calculated pH was 0.008–0.047 units higher in the study of Kuliński et al. (2014) whereas our results were too low compared to measurements. Dataset of Kuliński et al. (2014) is from November which means that surface seawater ecosystem was net heterotrophic unlike in our dataset. The CO_2 fluxes between the sea and the atmosphere in these two conditions are divergent.

Alkalinity in CO2calc model is simplified and does not contain all the possible components of the alkalinity. Dissolved organic matter *DOM* is ignored in the calculations. Due to low content of *DOM* in oceans it is reasonable to disregard its effect on alkalinity. By contrast, Baltic Sea is *DOM*-rich basin, and organic compounds are a significant part of alkalinity (Kuliński et al., 2014). A bulk dissociation constant representing acid-base properties of *DOM*, K_{DOM}, has been determined for Baltic Sea and that could be used for estimating organic alkalinity (Hammer et al., 2017; Kuliński et al., 2014).

Borates are important component of the total alkalinity and it has been considered in calculations of CO2calc. The problem with borates in the Baltic Sea is that the relationship between total boron concentration and salinity is not similar to that of the open ocean. In CO2calc model boron concentration is calculated with equation by Lee et al. (2010) which has been determined with open ocean measurements and it suggests that river water contains no boron at all. According to a study by Kuliński et al. (2018) the boron-salinity relation in Baltic Sea differs from the Lee's version especially when salinity is below 14 and pH is over 8.

The measurement campaigns in this study take place in spring and summer time. During that time measurement site is net autotrophic. To see how modelling works with autumn and winter conditions also, all year round data should be examined. Kuliński et al. (2014) measured carbonate system components in the Baltic Sea during November and the modelled results differed from modelled results in this study. Also, the relationship between temperature and inorganic carbon system components may change with all year-round dataset.

Large catchment area with *DOM*-rich river runoffs, hydrographical features, eutrophication and large seasonal changes makes Baltic Sea difficult to model. Local and temporal differences may be great. Alkalinity cannot be estimated reliably as simply as in the oceans. Therefore, it would be best to measure all the four components to get the most accurate picture of the inorganic carbon system. Model should be improved for Baltic Sea conditions before use. Equation for alkalinity should be modified taking account alkalinity components important in Baltic Sea, that is to say organic alkalinity and correct estimate for borates. Improving the model calls for measurements from all the components of the inorganic carbon system. In Utö, pCO_2 and pH is measured continuously, but alkalinity and *DIC* values are available only from discrete measurements. Maybe in future *DIC* and alkalinity too will be measured continuously. Due to local differences in the Baltic Sea, it may be difficult to put up a model that represents accurately the whole Baltic Sea.

6 CONCLUSIONS

The main objective of this thesis was to measure inorganic carbon system in Utö, Baltic Sea. Measuring equipment in Atmospheric and Marine Research Station worked well for carbonate system studies. Continuous measurements pH and pCO_2 gave data with high temporal resolution. Discrete measurements A_T and *DIC* completed the carbonate system dataset from the measurement campaign dates. The accuracy of the alkalinity stayed unclear due to non-standard reference sample and that should be checked.

Continuous measurements of seawater temperature and salinity supplemented the dataset. Our measurements from the summer 2017 support former results in the Baltic Sea. A strong correlation was found between alkalinity and *DIC*. Salinity correlated tightly with both alkalinity and *DIC*. Seawater pH and pCO_2 were clearly inversely related. During the spring and summer until mid-August the sea acted as a carbon sink based on the pCO_2 measurements. That is, seawater pCO_2 stayed below the atmospheric content of CO_2 and carbon flux was directed towards the sea.

To get the most accurate picture of the inorganic carbon system in Baltic Sea, it would be best to measure all the four measurable components of the system. Baltic Sea has a large catchment area with *DOM*-rich river runoffs and problems with eutrophication. Added with hydrographical features and large temporal and spatial changes in circumstances, Baltic Sea is difficult to model. If it is not possible to measure all the components, modelling should be performed with A_T or *DIC* and pH or pCO_2 values. Modelling with pH instead of pCO_2 gave a bit more reliable results. However, modelling results should be used with caution. Model could be improved for Baltic Sea conditions by taking account alkalinity components important in Baltic Sea. Rivers transport a lot of organic matter to Baltic Sea and therefore, organic component of alkalinity should be taken account with calculations. Also, borates cannot be estimated as reliably as in the oceans based on salinity. Improving and testing the model calls for measurements from all the components of the inorganic carbon system and from all the seasons.

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